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Department of Aquatic Sciences and Assessment
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Abstract

Sweden has had a long history of forestry activities together with pulp and paper operations. Historical discharges of organic-rich wastewater from pulp and paper factories have resulted in formation of large fiberbanks on the seafloor, which lately have been found to be contaminated with persistent organic pollutants (POPs). The aim of this study was to determine the levels of POPs in fiberbank sediments from two known contaminated sites (Väja and Sandviken) located in the Ångermanälven estuary in the county of Västernorrland, Sweden. The objective was to investigate the spatial distribution of POPs in these fiberbanks on both a horizontal and vertical axis. The sediment samples (n= 43) were collected on SGU's survey vessel Ocean Surveyor in autumn 2017. The sediment samples were extracted using a Soxhlet followed by a multilayered silica gel clean-up column, prior to instrumental analysis with GC-MS/MS. The sediment's concentration of hexachlorobenzene (HCB), 20 polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDT) and its transformation products (DDE and DDD) together referred to as DDX, were measured. At both locations, surface sediment samples (0-4 cm depth) generally presented low concentrations of POPs and organic carbon (TOC), likely due to recent sedimentation of fine clay material. At increased depth, contents of TOC, as well as, the levels of PCBs and DDX (sum of 6 DDT congeners) tended to increase. However, spatial distribution was found to be irregular within both fiberbank and fiber-rich sediment areas. The PCBs compositions, for each location, were found to be related to known technical grade products by using hierarchical cluster analysis. The toxicity of the target pollutants, found in the studied areas, was also assessed using the Norwegian quality standards for sediments. It was found that the HCB levels, for all the samples analyzed, were classified as having no effects on biota (Class II). In both areas, the state of the surface sediment, regarding the Σ *p,p'*-DDX and *o,p'*-DDT, was classified as good (Class II). However, as the sampling depth increased, many sites contained levels causing chronic effects of long-term exposure (Class III). Most of the levels of Σ_7PCB in surface sediment samples were classified as having no toxic effects (Class II) with few samples classified as causing chronic effects of long-term exposure (Class III). For both Sandviken and Väja, the levels of Σ_7PCB increased with sampling depth, and some sites contained levels which are classified as having acute toxic effects of short-term exposure (Class IV). To conclude, this study has contributed in generating important information about the distribution of hazardous contaminants in fiberbanks, and the risk on the immediate environments. The outcome from this study demonstrated how heterogeneous the contaminant levels can be in the vicinity of a pulp and paper factory. This should be taken into consideration when defining remediation strategies for fiber-impacted areas, like defining the site of a remediation project.

Keywords: PCB, DDT, HCB, fiberbank, fiber-rich sediment, sediment, Sweden, Västernorrland, Ångermanälven, Gulf of Bothnia, Baltic Sea.

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Popular science

The pulp and paper industry is an existential part of the Swedish economy; such that Sweden is considered one of the world leaders in this sector. The manufacturing of pulp and paper generates large volume of wastewater and prior to legislation in 1969, pulp and paper industries in Sweden used to discharge their wastewater, holding high content of wood and fiber cellulose into the aquatic environment. In many places has this cellulose and wood fiber material accumulated on the seafloor, and overtime, form so called fiberbanks. In the vicinity of a pulp and paper factory, the area affected by wastewater can be quite large; where the sediments cellulose composition follows a gradient from pure fibers (fiberbanks), fiber-rich sediments and less affected sediments. This study has looked into a group of substances referred to as persistent organic pollutants (POPs) because they are hard to degrade, they can accumulate in the fat of living organisms and they are toxic. The pollutants analyzed in this study were hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDT) and its transformation products (DDE and DDD), together referred to as DDX, and 20 polychlorinated biphenyls (PCBs). All those substances were employed in different products such as pesticides, fungicides, wood-preservative and various industrial devices and would eventually be a part of the wastewater. Although the production and use of these contaminants were banned in Sweden in the 1970s, they are still found in the environment. Chemical analysis was conducted to determine the concentrations of those contaminants in the fiberbanks areas of Sandviken and Väja, in the county of Västernorrland. Overall, the concentration of HCB in the fiberbanks and the fiber-rich samples was found to be low. For the DDX compounds, their concentration varied from low to medium levels, in both type of sediments. The concentration of PCB ranged from low to high, generally increasing with depth of sampling. A distribution ratio was made for the PCBs and DDX compounds to represent the fraction of each contaminant in a sample. This distribution ratio showed that the composition of contaminants for all the samples was generally the same, revealing a related source of pollution. The PCB compositions of the samples were further analyzed and compared to existing technical grade products used by the industry. In Sandviken, it was found that nearly all the samples matched the composition of Kanechlor KC-500 and in Väja, technical grade product resembling the composition of the samples were Clophen A60, Aroclor 1260 and Kanechlor KC-600. A risk assessment was conducted using the Norwegian quality standard for water, sediment and biota to classify the ecotoxicological effects of the known concentrations in the fiberbank areas. Generally, the surface sediments presented good status with all contaminants levels showing no effects to living organism. With increasing depth, a few sites exhibited DDX concentrations with levels causing chronic effects of long-term exposure. For PCBs, most sites displayed contents ranging between chronic effect of long-term exposure and acute effects of short-term exposure. In conclusion, the data collected in both Sandviken and Väja, regarding differences in POPs concentrations between fiberbank and fiber-rich sediments, was not convincing enough to justify a distinction between the two contaminated fibrous sediments, on a risk assessment point of view. Finally, this study demonstrated how heterogeneous the contaminants levels can be in the vicinity of a pulp and paper factory.

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List of abbreviations

CEPI	Confederation of European Paper Industry
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethene
DDT	Dichlorodiphenyltrichloroethane
Σ_6DDX	Sum of the six DDT related compounds analyzed (i.e. *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD)
DW	Dry weight
FR	Fiber rich sediment (sample name abbreviation)
GC	Gas chromatograph
HCB	Hexachlorobenzene
IS	Internal standards
K_{OW}	Octanol-water partition coefficient
LOD	Limit of detection
LOI	Loss on ignition
LOQ	Limit of quantification
MS	Mass spectrometer
OC	Organic carbon
OPB sampler	Orange peel bucket sampler
PCB	Polychlorinated biphenyl
Σ_{20}PCB	Sum of the 20 PCBs analyzed (i.e. PCB-28, -52, -77, -81, -101, -105, -114, -118, -123, -126, -138, -153, -156, -157, -167, -169, -170, -180, -189, -209)
Σ_7PCB	Sum of seven indicator PCBs (i.e. PCB-28, -52, -101, -118, -138, -153, -180)

POP	Persistent organic pollutant
Q	Refers to the sites of Sandviken in the sample name abbreviation
R	Refers to the sites of Väja in the sample name abbreviation
RS	Recovery standard
S/N	Signal to noise ratio
S	Less affected sediment (sample name abbreviation)
SD	Standard deviation
Swedish EPA	Swedish Environmental Protection Agency
SGU	Geological Survey of Sweden (Sveriges Geologiska Undersökning)
SLU	Swedish University of Agricultural Sciences (Sveriges lantbruksuniversitet)
USEPA	United States Environmental Protection Agency
v/v	Volume per volume

Introduction

The province of Västernorrland has had a long history of forestry activities together with pulp and paper operations. From the end of the 19th century until the first implemented environmental legislation in 1969, discharge of wastewater, holding high content of wood and fiber cellulose, into adjacent coastal marine environment was custom to the industry. In many places, this fiber material accumulated on the sea floor and formed large banks, referred to as fiberbanks. Along the coast of Västernorrland, such fiber material is covering more than 1.5 km^2 of the sea floor (Apler *et al.*, 2014).

The fate of fiberbanks has been neglected in the past within marine and water quality management. Knowledge of recirculation of historical discharged persistent organic pollutants (POPs) and heavy metals in the Gulf of Bothnia is now prominent. In spite of all the measures and strategies to reduce the inputs of such contaminants to the Gulf of Bothnia, and not to mention the Baltic Sea, these pollutants still circulate in the aquatic ecosystem and can occur at high concentration in recently deposited sediments (Apler & Josefsson, 2016). Furthermore, the coastal area of Västernorrland is also known to experience a rapid land uplift, around 8 mm per year (Apler, 2018). Consequently, fiberbanks are getting closer to the sea surface, where they will be more exposed to erosion caused by waves, currents and propeller wash by coastal traffic, which can result in re-suspension, dispersion and re-introduction of buried contaminated material to the ecosystem.

The creation of the project known as the *Fiberbank project* in 2010 was carried out by the Geological Survey of Sweden (SGU) in collaboration with the County Administrative Board of Västernorrland in order to assess the status and the fate of these fiberbanks (Apler *et al.*, 2014). This project also aimed to serve as a base for further planning and implementation of mitigation and remediation strategies of areas judged as a menace to the environment. The main objectives of the *Fiberbank project* were to survey and map the spatial distribution of fibrous sediment using hydro-acoustic techniques and to estimate the levels of contaminants of those sites by sediment sampling. Chemical analysis was also carried out to assess the influence of local sources of fibrous pulp emissions and the concentration of metals and organic pollutants classified according to the Swedish Environmental Protection Agency's (Swedish EPA) criteria for environmental quality, Coast & Sea (Apler *et al.*, 2014).

In addition to the *Fiberbank project*, was several research initiatives initiated with the aim of increasing knowledge on contaminants presence and fate in fiberbanks. The research project TREASURE studies the dispersal of old hazardous contaminants from fiberbanks along the Swedish coast which jeopardize the health of the Baltic Sea. The Ångermanälven estuary was chosen as the study area in TREASURE. The goal of the project is to generate quantitative knowledge about the physical and chemical stability of the fiberbanks, which can be used by environmental managers in their decision making, regarding remediation strategies for fiberbanks.

Aim and objectives

This research project was carried out as part of TREASURE and the overall aim of this study was to investigate the spatial distribution of POPs in fiberbanks from two known contaminated sites (Väja and Sandviken), located in the Ångermanälven estuary, in the county of Västernorrland, Sweden. The first objective was to measure the levels of POPs, on both a horizontal and vertical axis, to be able to compare concentration of POPs in surface sediment with deeper sediment and the distance from the pulp factories. This information is important for defining the area for potentially future remediation. The second objective was to compare the levels of POPs with the Swedish environmental assessment criteria for sediment and to evaluate the ecotoxicological risk for aquatic and sediment dwelling organisms by using the Norwegian environmental quality standards for sediment.

Background

Pulp and Paper Industry

Overview

The pulp and paper industry is an essential industry that supply indispensable product to the world's population. Paper and its related product have such a broad functional use e.g. to store, collect and distribute information, for packaging and transportation, for hygienic purposes, etc. (Suhr *et al.*, 2015). The largest production of pulp comes from North America (37.4%), followed by Europe (25.4%) and then Asia (23.1%) (Suhr *et al.*, 2015). In Europe, the countries contributing most to the manufacturing of pulp are Finland and Sweden, together representing 57% of the total pulp production (Suhr *et al.*, 2015). The forestry industry is one of the most important sector of economic in Sweden (The Swedish Forest Industries, 2015). It is logical, since the country has 70% of its land area covered with forest, which represents 28 million hectares of forest (Swedish Wood, 2012). Moreover, the Swedish forestry industry employs, both directly and indirectly, about 100 000 people and possesses 50 pulp and paper mills and 120 sawmills in the country (The Swedish Forest Industries, 2016).

There are five steps required to make paper and each step can be carried by a variety of methods. Those procedures can be described as followed:

1. *Debarking* removes the bark containing tannins, resins acids and other impurities from the raw timber and shreds the plant fiber into small chips (Ali & Sreekrishnan, 2001 & Pokhrel & Viraraghavan, 2004).
2. *Pulping* is a process removing most of the lignin and hemicellulose content from the raw material, yielding a cellulose-rich product known as pulp (Ali & Sreekrishnan, 2001).
3. *Bleaching* is use to turn the brown pulp into the required color. Many different bleaching agents are employed by the industry like chlorine, chlorine dioxide, ozone, etc.
4. *Washing* or alkali extraction stage removes the bleaching agent as well as color from the pulp using caustic soda.
5. *Paper and paper products* are made by mixing the final pulp product with a filling agent such as clay, calcium carbonate or titanium dioxide together with a sizing agent like starch and rosin.

Effluents discharge

Water is used extensively in the manufacturing of paper, from debarking to the final product, to reappear as an effluent. The pulp itself is said to represent approximately 40-45% of the original weight of the wood, meaning that substantial volume of organic matter is held by the wastewater (Pokhrel & Viraraghavan, 2004). The characteristics of those effluent can vary according to the type of processes employed, type of plant material, technology, internal recirculation, cleaning treatment, etc. (Pokhrel & Viraraghavan, 2004). Effluents from pulp and paper mills factory can be threat to aquatic environment due to their high toxicity. Those toxic chemicals can be naturally occurring within the product or together with anthropogenic compounds, which are influenced and released during the papermaking procedures (Ali & Sreekrishnan, 2001).

Some of the halogenated compounds (e.g. polychlorinated dibezo-*p*-dioxins and polychlorinated dibenzofurans) that have been found in pulp and paper effluents (Ali & Sreekrishnan, 2001) are classified as persistent organic pollutant (POPs), according to the Stockholm convention (UNEP,

2004). POPs are toxic compounds with a strong ability to resist degradation, thus they can persist for a long time in the environment and undergo long-range transport. POPs are fat soluble and can biomagnify in the food chain resulting in elevated concentrations in top predators (UNEP, 2004). Since they are classified as priority pollutants by the United Nations Environmental Program (UNEP, 2004), POPs are thoroughly monitored in the environment.

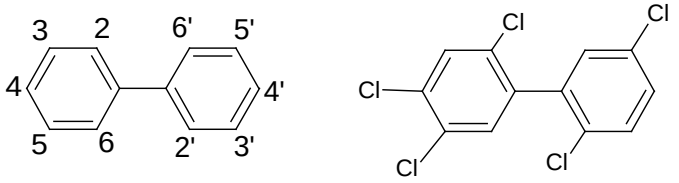
Target compounds

This study has focused on persistent organic pollutants (POPs) that has been found in fiber contaminated areas inventoried in previous studies by the Swedish Geological Survey (SGU) (Apler, 2018). The contaminants of concern include polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and its transformation products; dichlorodiphenyldichloroethene (DDE) and dichlorodiphenyldichloroethane (DDD). Hexachlorobenzene (HCB) was also included in this study as it has been found in many fiber-contaminated areas. More information about these POPs is given in the following sections.

PCB

The production of polychlorinated biphenyls (PCBs, Figure 1) started in 1929 and have been used in various industrial applications such as dielectric fluids in transformers and capacitors, hydraulic fluids and lubricants, where PCBs resistance to both acids and alkalis combined with its heat stability was use full. Other uses for PCBs has been as surface coating, flame retardants, plasticizers, inks, adhesives and paints (CICAD, 2003). However, the use of PCB is nowadays banned under the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2004)

PCBs consist of in total 209 chlorinated congeners, which are numbered according to the positions of the chlorine atoms on the biphenyl rings (Figure 1) (Ballschmitter *et al.,1993*). In the environment, the various congeners of PCBs adsorb strongly to soil and sediment depending on their degree of chlorination (CICAD, 2003). The persistency and hydrophobic properties of these substances results in their accumulation in sediment and living organism of aquatic ecosystems, where they can cause a variety of toxicological effects in both animals and humans (HELCOM, 2013).



PCB-101

Figure 1 *Chemical structure of a biphenyl with numbers showing the position of the chlorine atoms. The numbering system is exemplified by 2,2',4,5,5'-hexachlorobiphenyl (PCB-101).*

DDT

Dichlorodiphenyltrichloroethane (DDT, Figure 2) was introduced as an insecticide on the market in the 1940s. The efficiency and popularity of DDT to control agricultural and forest pests corresponded to its long action-time, low acute mammalian toxicity and low cost (Turusov *et al.*, 2002 & EFSA, 2006). DDT has also been of great help to control disease vectors such as mosquitos carrying malaria and head lice, fleas and ticks carrying typhus and DDT is still used in some countries where malaria is still a threat (EFSA, 2006). However, the extensive use of DDT during the 1950's and 1960's along with the compounds persistency to undergo degradation resulted in elevated concentrations in the environment. DDT is toxic to aquatic microorganism, fishes, amphibians and birds, and in the 1960's, the adverse environmental effects of DDT began to reveal themselves (EFSA, 2006). In Sweden, the white-tailed sea eagle (*Haliaeetus albicilla*) nearly faced extinction in the 1960-70's due to reproductive failure, an effect found to be associated with exposure to dichlorodiphenyldichloroethene (DDE), a transformation product of DDT (Helander, 1985). Hence, Sweden was the first country to ban the use of DDT in 1970 (Hayes, 1969; Sweden Environmental Protection Agency, 2011), soon followed by other countries and was among the first compounds to be listed under the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2004)

In the environment, DDT can be transformed through reductive dechlorination into dichlorodiphenyldichloroethene (DDE, Figure 2) and dichlorodiphenyldichloroethane (DDD, Figure 1), either microbially mediated or by chemical reactions. In soils, DDT is strongly adsorbed to organic matter and slowly starts to degrade into DDE by dehydrochlorination under aerobic conditions and DDD under anoxic conditions mainly through reductive dechlorination (Aislabie *et al.*, 1997 & EFSA, 2006).

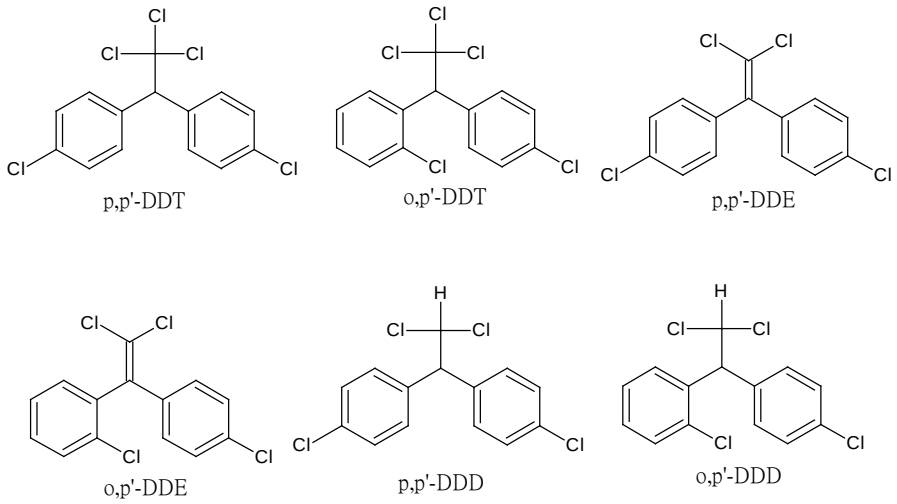


Figure 2 *Chemical structures of DDT (p,p'-DDT and o,p'-DDT) and its transformation products DDE (p,p'-DDE, o,p'-DDE) and DDD (p,p'-DDD, o,p'-DDD).*

HCB

Hexachlorobenzene (HCB, Figure 3) was introduced on the market in 1945 and used as a pesticide (EFSA, 2006). The major application of HCB was as seed dressing to prevent the growth of fungi on crops (EFSA, 2006). In the forestry industry, HCB has been commonly used as a wood-preserving agent before the lumber would be processed. Although its use was discontinued in most countries in the 1970s, and listed under the Stockholm Convention on Persistent Organic Pollutants (POPs), it continues to be released in the environment from different sources. HCB can be released as a by-product when chlorinated compounds are fabricated, incomplete combustion, landfill leaching and waste from manufactures of chlorinated products (EuroChlor, 2005 & EFSA, 2006).

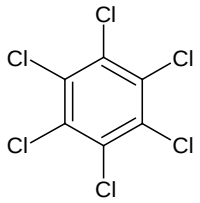


Figure 3 *Chemical structure of hexachlorobenzene (HCB).*

Once released to the atmosphere, HCB can exist in both vapour phase or in association with particles (Eisenreich *et al.*, 1981). Although its resistance to degradation, HCB does undergo photolytic degradation, when in the vapour phase, with an estimated half-life of about 80 days (Mill and Haag, 1986). Consequently, HCB can be carried over long distances, far away from the original source of emission, and bioaccumulate in fatty tissues of living organisms (EFSA, 2006).

Hexachlorobenzene is very persistent in soils and sediments where its mobility, transport and degradation are reduced mainly due to its strong sorption to organic matter (EuroChlor, 2005 & EFSA, 2006). Toxicological effects of HCB exposure on experimental animals can induce disturbances in the immune system, reproductive system, tumours in the liver, kidney and endocrine organs (EFSA, 2006). These results lead the International Agency for Research on Cancer (IARC), to classify HCB as a possible human carcinogen (group 2B) (EFSA, 2006).

Material and Method

Fiberbank areas studied

The two fiberbanks areas studied are located in Ångermanälven river estuary in the county of Västernorrland, Sweden (Figure 4). Historically, Västernorrland county has been operating many pulp and paper factories since the end of the 19th century (Apler *et al.*, 2014). Those factories also have a long history of discharging their untreated wastewater, holding high cellulose fiber content and wood residue, into the coastal marine environment (Apler *et al.*, 2014). This extensive volume of fibrous emissions created banks of pure fibers deposited on the sea floor and fiber-rich sediment where fiber materials were mixed with the natural sediments.

One fiberbank is situated close to Väja Kraft pulp mill, a sulphate pulp factory still in use today, which began its operations during 1914-1915. The predicted production capacity, at that time, was to meet 12,000 tonnes of unbleached pulp annually and gradually increase until it reached about 100,000 tonnes per year, in 1969 (Paler, *et al.*, 2014). Until 1955, the cellulose rich wastewater created by the pulping process at Väja was released in the estuary, without any cleaning procedure. According to investigations performed by the Swedish Geological Survey (SGU), the fiberbank in Väja covers an area of approximately 70,000 m^2, has a thickness of at least 6 m and consists mostly of cellulose fibers (Apler *et al.*, 2014). The second fiber bank is located close to Sandviken old Kraft pulp mill. This sulphate pulping factory was founded in 1929 and was manufacturing unbleached pulp (Apler *et al.*, 2014). However, the factory closed its door and was demolished on site and covered in 1979. The fiberbank in Sandviken covers approximately 55,000 m^2, has a thickness of at least 6 m and consists mainly of wood fibers and wood chips (Apler *et al.*, 2014).

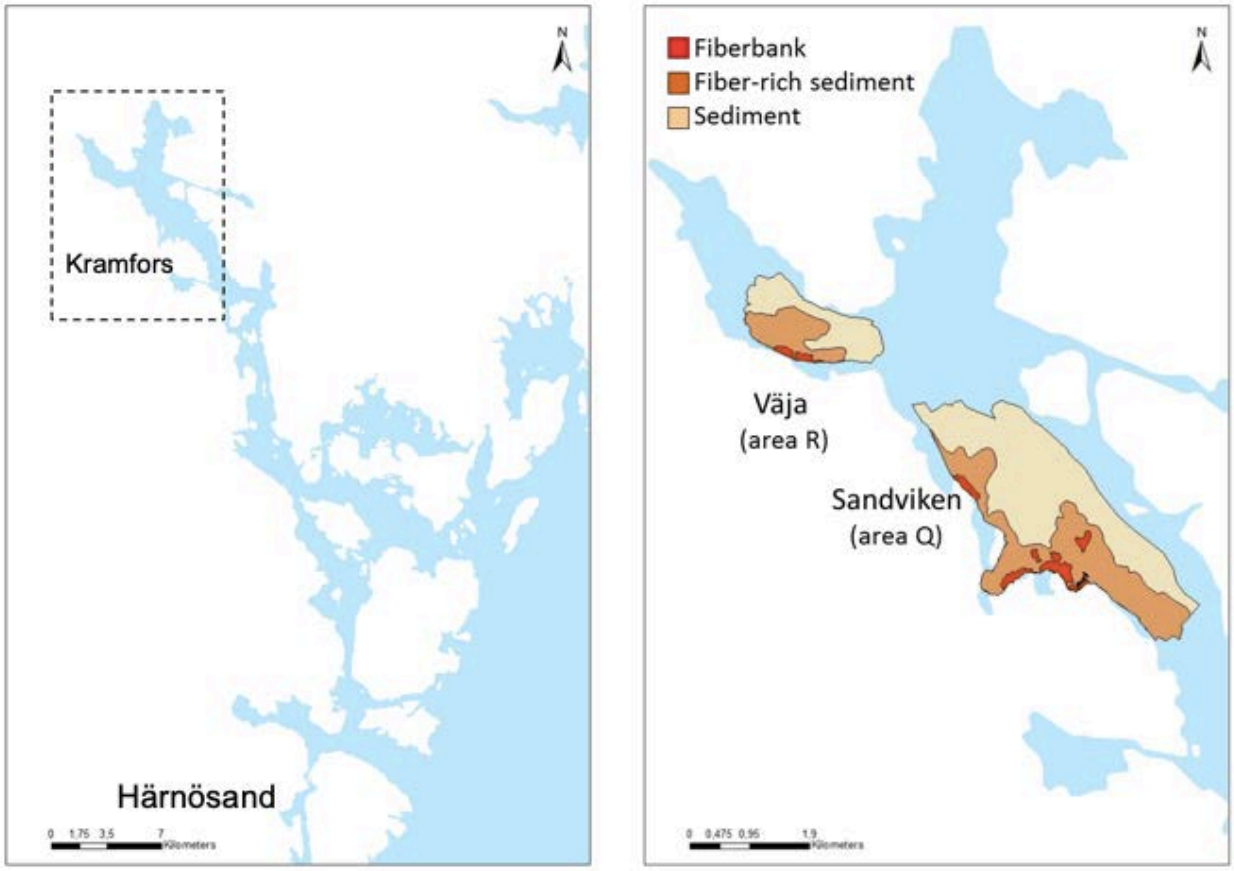


Figure 4 *Ångermanälven river estuary (Västernorrland, Sweden) and the two fiberbank sites: Väja and Sandviken. Fiberbank areas are coloured red, fiber-rich areas light orange and sediment areas in beige.*

Laboratory equipment and procedures

Sample collection

The collection of sediment samples was performed from the SGU's survey vessel Ocean Surveyor, in autumn 2017. To collect the sediments, a Gemini core sampler (Gemax) was mainly used but when softer and unconsolidated sediment was found, a large box corer (L30 x W30 x

H50) was used for sampling. The height of the collected sediment sample was measured on board on Ocean Surveyor and sediment was sampled for chemical analysis from parts corresponding to the sea floor surface (0-4 cm sediment depth) and deeper sediment (max 50 cm sediment depth). In Sandviken, 6 sampling sites were located in the fiberbank, 2 in the fiber-rich area and one in the natural sediment outside the fiber-rich area (site Q2); an area not visibly affected by fibers (Figure 5). In total, 19 samples were taken for chemical analysis from Sandviken, including one duplicate sample (site Q15). Detailed sampling information is presented in Table 1. All samples were stored frozen (-18 °C) until chemical analysis. In Väja, 14 sites were sampled (Figure 6); 5 sites corresponded to the fiber-rich sediment, whilst the remaining 9 sites were within the fiberbank. In total, 24 samples were taken for chemical analysis in Väja, including one duplicate sample (site R17).

Table 1 *Sample site and depth of sampling for each location according to the SGU map. SED = pure sediment location, FR = fiber-rich sediment location, Sample site with no acronym = fiberbanks sediment location. The asterix (*) indicate samples collected in duplicate.*

Sandviken		***Väja***	
Sample Site	**Sample Depth (cm)**	**Sample Site**	**Sample Depth (cm)**
$Q02_{SED}$	0-4	R13	0-4
$Q02_{SED}$	28-32	R13	16-20
Q13	0-4	R14	0-4
Q13	28-32	R14	24-28
Q14	0-4	R15	0-4
Q14	16-20	R15	16-20
Q15*	0-4	R16	0-4
Q15*	17-21	R16	15-18
Q15	17-21	$R17_{FR}$	0-4
Q16	0-4	$R17_{FR}$*	16-20
Q16	12-16	$R17_{FR}$*	16-20
Q17	0-4	R18	15-50
Q17	20-25	$R19_{FR}$	0-4
$Q18_{FR}$	0-4	$R19_{FR}$	24-28
$Q18_{FR}$	24-28	$R20_{FR}$	0-4
Q19	0-4	$R20_{FR}$	28-32
Q19	28-32	R21	0-25
Q20	0-4	$R22_{FR}$	0-50
Q20	16-20	R23	0-50
		R24	0-50
		R25	0-13
		$R26_{FR}$	0-4
		$R26_{FR}$	28-32

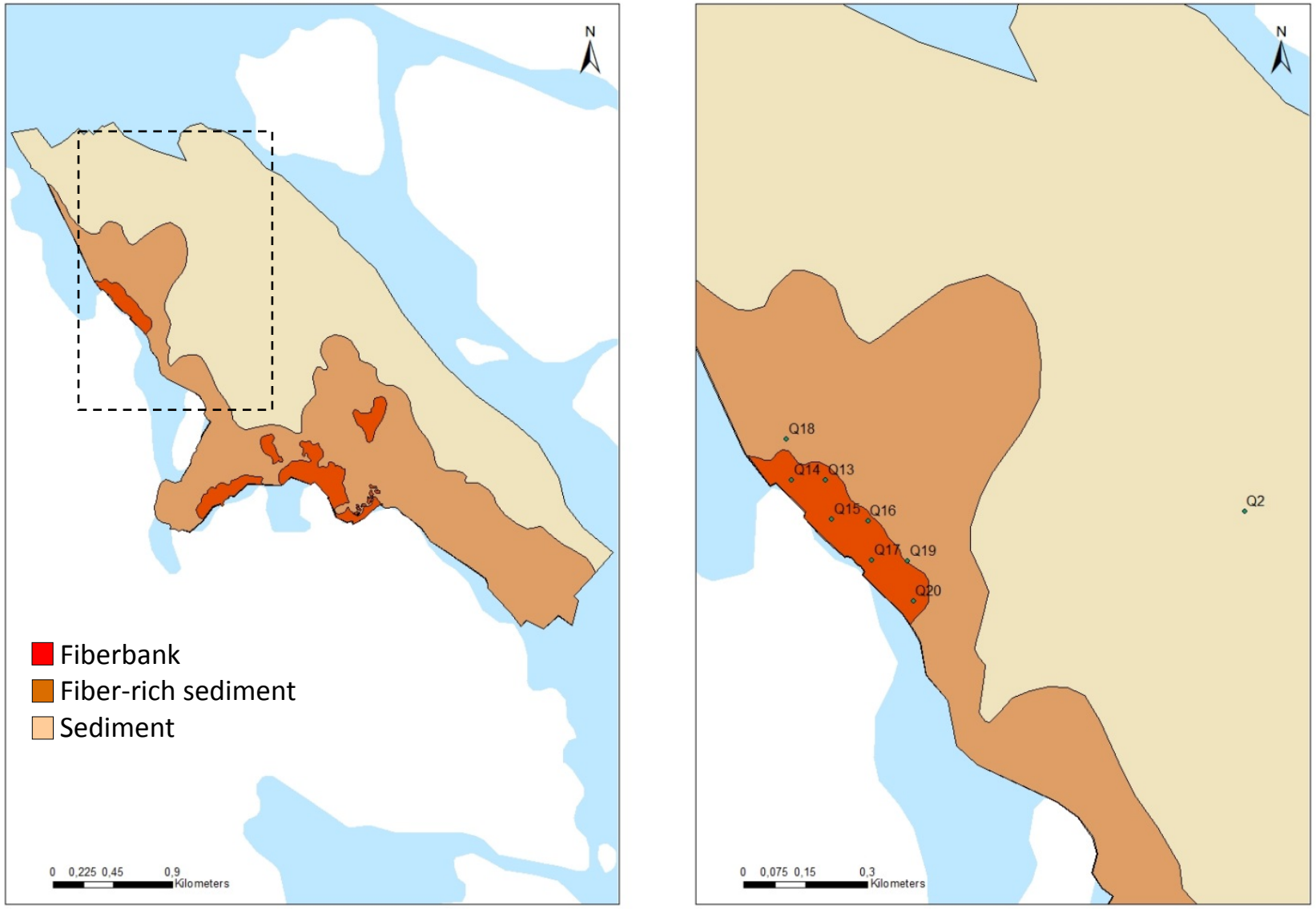


Figure 5 *Sample sites in Sandviken: Fiberbank areas are colored red, fiber-rich areas in light orange and sediment areas in beige.*

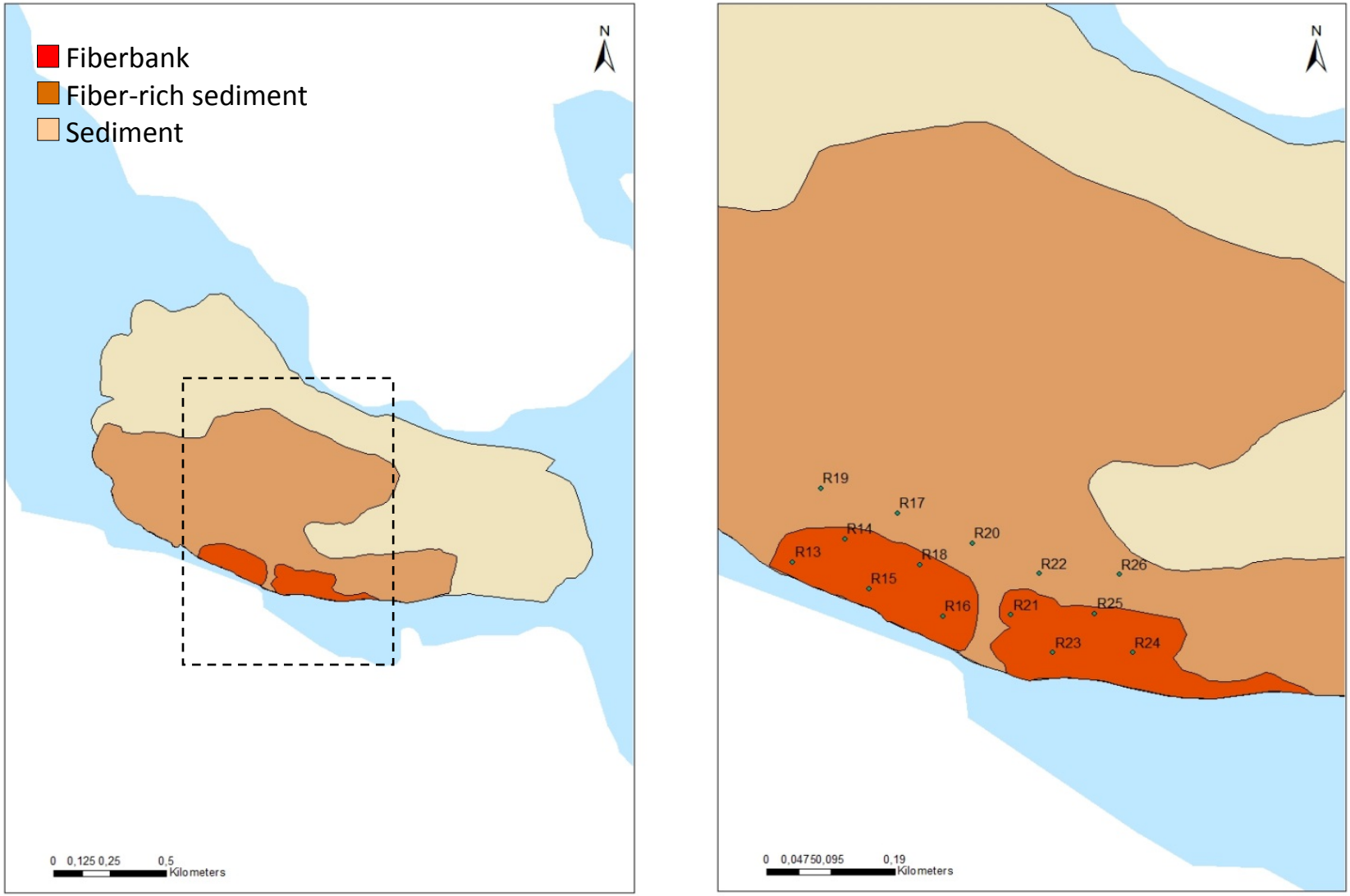


Figure 6 *Sample sites in Väja: Fiberbank areas are colored red, fiber-rich areas light orange and sediment areas in beige.*

List of analytes and chemicals

In this study, 20 PCBs (CB-28, -52, -77, -81, -101, -105, -114, -118, -123, -126, -138, -153, -156, -157, -167, -169, -170, -180, -189, -209), 2 DDT (*o,p'*-DDT and *p,p'*-DDT), 2 DDE (*o,p'*-DDE and *p,p'*-DDE) and 2 DDD (*o,p'*-DDD and *p,p'*-DDD) and HCB were analyzed. The native compounds used as authentic reference standard are listed in Appendix (Table 9) including their acronym, compound name, origin, purity and log K_{OW}. Whereas isotope-(^{13}C)-labelled compounds used as internal standards or recovery standards are listed in Appendix (Table 10).

In the result and discussion part of this report, the sum of all 20 PCBs are referred to as Σ_{20}PCB, and the sum of the seven PCB indicator (CB-28, -52, -101, -118, -138, -153, -180) abbreviated as Σ_7PCB. Whereas the sum of the 2 DDT, 2 DDE and 2 DDD is abbreviated as ΣDDX.

The chemicals and solvent used in extraction and clean-up of the sediment samples are listed in Table 2, along with certain specifications and their fabricants. The sodium sulphate, silica and glass wool were heated overnight (at 400 °C) and stored in a desiccator until use.

Table 2 *List of chemicals used, their specification and origin. Origin abbreviation: MK (Darmstadt Germany), SA= Sigma-Aldrich (St. Louis, USA), VWR (Leuven, Belgium).*

Name of chemical	Specification	Origin
Acetone	SupraSolv®	MK
normal-hexane (n-hexane)	SupraSolv®	MK
Dichloromethane	SupraSolv®	MK
Hydrochloric acid	30% SupraPur®	MK
Copper	ACS reagent, granular, 10-40 mesh, 99.90%	SA
Silica	(0.063 – 0.200 mm)	MK
Sulphuric acid	96%	VWR
Sodium sulphate anhydrous	AnalaR NORMAPUR	VWR
Extraction thimbles	501, cellulose	VWR
Glass wool		SA

Sample extraction and clean-up

Prior to the extraction, the sediment samples (n = 43) were first freeze-dried to remove water and then stored in a freezer (at a temperature of -18 °C). The sediment samples were then extracted using Soxhlet. In addition, 3 sediment samples (Q14, Q17 and R26) were extracted and cleaned up in triplicate. Procedural solvent blanks were also included as quality assurance (n = 6). The chosen methodology for extraction was based on the US EPA Soxhlet extraction method:3540C, which refers to a procedure for extracting non-volatile and semi-volatile organic compounds from solids (US EPA Method 3540C, 1996). Prior to each batch of samples being extracted, all Soxhlet equipment; including the Soxhlet extractor, the cellulose thimble and the 500 mL round bottom flask, were cleaned from impurities by running the Soxhlet overnight with acetone: *n*-hexane (200 mL, 1:1, v/v).

To begin the extraction, freeze-dried sediment samples (approx. 2.5 g) were placed into the pre-cleaned extraction cellulose thimbles and spiked with (^{13}C)-labelled internal standards (see table 10 in the appendix for further information). The spiked samples were covered with glass wool

and then placed in the cleaned Soxhlet extractors. Each sample was extracted with a renewed volume of 200 mL acetone: *n*-hexane (1:1, v/v) for 20-24 hours (Figure 7). Each sample extract was evaporated down to approximately 1 mL using a TurboVap II evaporation system (Biotage, Sweden), where a heating bath (41 °C) and gentle flow of nitrogen (N_2) gas is used to accelerate the evaporation.

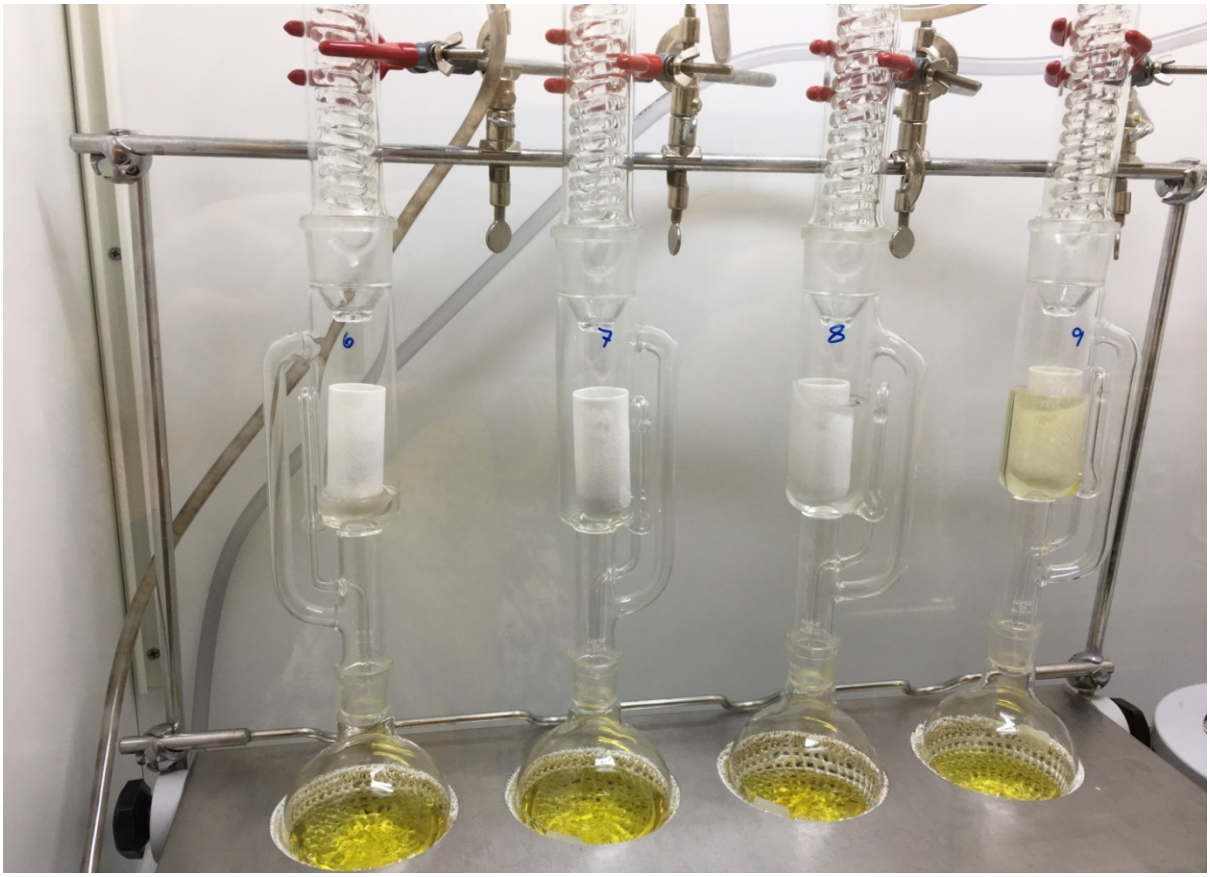


Figure 7 *Soxhlet extraction apparatus in use.*

The concentrated extracts were then cleaned up. To begin with, the concentrated extracts were placed in glass vials together with activated copper to remove sulfur from the solution. This clean-up stage follows the US EPA method 3660B for sulfur removal which aim is to reduce the interference of sulfur when operating gas chromatography instrument (US EPA, Method 3660B, 1996). The copper was activated prior to use, by rinsing three times for each step, in the following order; hydrochloric acid 30%, followed by Milli-Q water, acetone and *n*-hexane. Once activated, the copper (approx. 2 g) was added to the extract and was vigorously mix for about one minute with a Vortex mixer. The addition of activated copper to the sample was repeated until the newly added copper remained shiny (Figure 8).

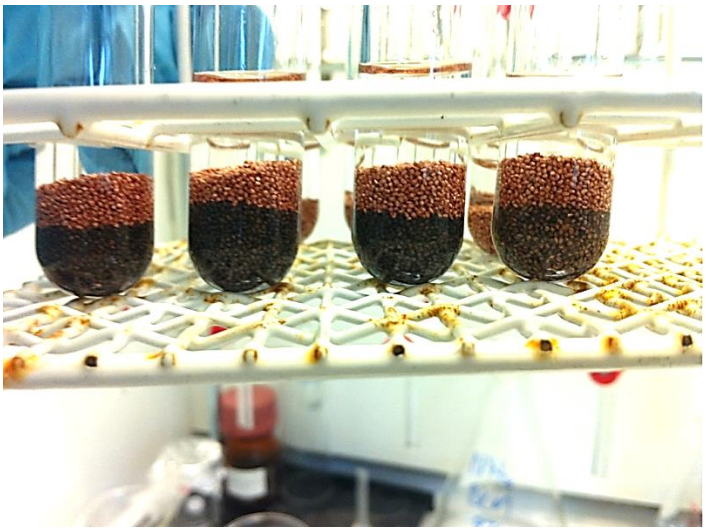


Figure 8 *Sulfur removal with activated copper. Sulfur give copper a blackish colour on its surface. Copper was added until copper granules remained shinny.*

After sulfur removal, the sample extracts were put through a multi-layered column made of; from top to bottom, sodium sulphate (3 g, Na_2SO_4), sulfuric acid silica gel (6 g, 40% H_2SO_4: SiO_2), activated silica (3 g, SiO_2) and glass wool (Figure 9).

Before adding the samples, the multi-layered columns were rinsed with *n*-hexane with a volume corresponding to two times the height of the column. The samples (including the copper) were then added to the columns and the test tubes were rinsed three times using a solution of dichloromethane: *n*-hexane (1:5, v/v) and also added to the columns. The samples were next eluted with dichloromethane: *n*-hexane (60 mL, 1:5, v/v) into TurboVap flasks for evaporation down to 1 mL. This clean-up step was repeated twice due to high level of co-extractives in all samples. Finally, (^{13}C)-labelled recovery standard (RS) was added and the samples transferred into gas chromatography (GC) vials and evaporated down to 100 µL using an N-Evap nitrogen evaporator.

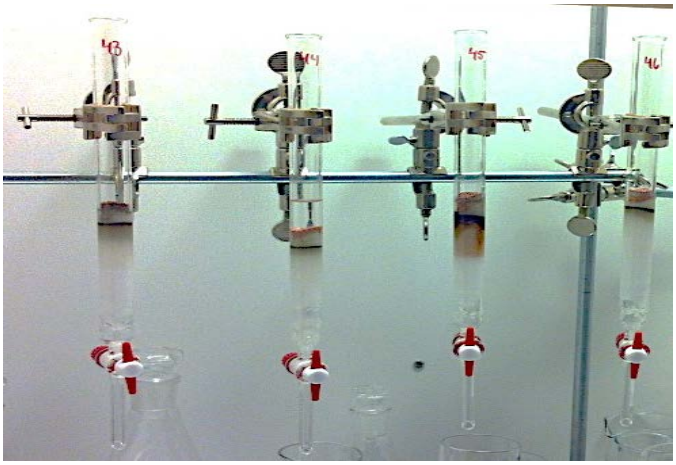


Figure 9 Clean-up stage of samples through a multi-layered silica column.

Dry weight and organic carbon analysis

The samples dry weight and loss of ignition (LOI) was measured gravimetrically after the samples were heated in an oven at 105 °C for 24 h and 550 °C for 4 h, respectively. The content total organic carbon (TOC) was determined by the Department of Soil and Environment, SLU, using the Swedish standard procedure SS-ISO 10694. The procedures involve dry combustion and elemental analysis using a TruMac instrument (Leco Corporation, St-Joseph, USA).

GC-MS/MS

The analysis was performed on a gas chromatograph (GC 7890A, Agilent Technologies) coupled to a triple quadrupole mass spectrometer (7010 GC-MS/MS Triple Quad, Agilent Technologies). The GC was equipped with an autosampler (7693, Agilent Technologies) to provide fast and reliable injections. The injector was set in a split-less mode, held a temperature of 275 °C and an injection volume of 2 μL was used. A DB5 capillary column (60 m x 250 μm id x 0.25 μm, Agilent Technologies) was used to separate the analytes in the GC. A constant flow of helium was used as a carrier gas in the capillary column, at a flow rate of 2 mL min^{-1}. The temperature program of the GC oven started off at 190 °C, which was held for two minutes, then increased by 3 °C/min until 250 °C was reached. Thereafter, the temperature increased from 6 °C/min up to 310 °C, held for one minute.

The MS/MS used the electro ionization (EI) mode at 70 eV. The ion source temperature was held at 300 °C and the transfer line between GC and MS/MS set at 310 °C. Nitrogen (N_2) was used as a collision gas and helium (He) as quench gas in the collision cell. The multiple reaction monitoring (MRM) was used to monitor the two transitions of the target compounds. Identification and quantification of target compounds was done using authentic reference standards (Table A1). Finally, the data evaluation was performed with Agilent MassHunter Quantitative Analysis (for QQQ).

Quality assurance & quality control

During Soxhlet extraction, a solvent blank was added to every batch of samples (n = 6). Those procedural solvent blanks were treated in the same fashion as the sediment samples for quality control. The blank from the second batch (B2) of experiment was not analyzed due to potential contamination of water, thus it was not further processed in the experiment. Before the extraction started, the sediment samples were spiked with (^{13}C)-labelled internal standards at known amounts, to correct for losses of target compounds during sample handling. Since the internal standards used behaves the same way as the target compounds, the loss of internal standard thus reflects the loss of target compounds and corrects for it. Those isotopes labelled compounds used as internal standard or recovery standards are listed in table A2 in the appendix.

Prior to the GC-MS/MS analysis, a (^{13}C)-labelled recovery standard was added in known amounts to the samples in order to assess the performance of the method and to calculate the recovery of the internal standard. The recovery was calculated, as showed in equation 1. The recovery of the isotopic labelled internal standards were on average 52 % for HCB, 80 % for PCBs, 88 % for *p,p'*-DDT and 85 % for *p,p'*-DDE.

$$R(\%) = \frac{A_{IS(sample)}}{A_{IS(calibr\ sol)}} \times \frac{A_{RS(calibr\ sol)}}{A_{RS(sample)}} \times 100$$

Equation 1 *Recovery method calculation*

During the quantitative analysis, a limit of detection (LOD) was set in order to distinguish the presence of the target compound from the analytical noise. The LOD applied in the chromatographic method adopted a signal-to-noise ratio (S/N) of 3, meaning that the peak signature of a compound had to be at least 3 times higher than the background noise from the instrument to be considered detected. What's more, the limit of quantification (LOQ) was seated at the lowest concentration of the calibration solution. Hence, in order for the analytes to be quantified, their concentrations needed to exceed the LOQ value of 0.02 ng absolute. Furthermore, the calculated concentration of each analytes was corrected by subtracting the average concentration of the blanks from the samples, to compensate for unintentionally introducing the target compounds to the samples while handling them.

Statistical analysis

For statistical analysis and for calculations of geometric mean (GM) and sum, values below LOQ were assigned a value of LOQ/2. The statistical analysis was performed using Soft Independent Modelling by Class Analogy (SIMCA, version 14.0.0.1359, Umetrics, Umeå, Sweden) was employed as a statistical method for classification of data. The product of this statistical analysis was used to illustrate the arrangement of the clusters produced by hierarchical clustering, also commonly known as a dendrogram.

Results and Discussion

Sediment organic carbon content

The total organic carbon (TOC) content found in the sediment samples from Sandviken and Väja are presented in Figure 10 and 11, respectively.

In Sandviken, the TOC geometric mean was 2.1 % in surface sediment samples (0 to 4 cm depth), represented in blue in figure 10. Sample represented in green (12 to 20 cm depth), demonstrated a range of TOC from 2.4 to 24 %. In the yellow group (24 to 32 cm depth), the TOC ranged from 2.1 to 31 %. In the yellow group, site Q02 does not belong to the fiberbanks itself as it was sampled far away from the fiberbank (Figure 5). Nevertheless, it does establish a reference of TOC in a more natural sediment, not visibly affected by fibrous depositions from the sulfate pulp mill in this area. The results in Sandviken show that surface sediment contains less TOC than samples taken at deeper depth in the fiberbank, due to recent sedimentation of fine material such as laminated clay (Apler *et al.*, 2014).

In addition, the samples from site Q13 and Q18 (yellow group) demonstrate a much lower TOC than site Q19. Their TOC are also lower than samples from site Q14, Q16 and Q20, from the green group. When referring those sites to the fiberbank map (Figure 5), one can see that all the samples from the green group lies well within the red boundary of the fiberbank, whereas Q18 lies in the fiber-rich area, Q19 on the border of the two boundaries and Q13 in the fiberbank area. On the other hand, duplicate samples from site Q15 (green group) do not show a TOC content expected from a site within the center of the inventoried fiberbank (Figure 5), but rather a TOC of a sediment sample such as the site Q02 (yellow group). The sites Q13, Q15 and Q19 shows

that there can be great spatial variation of TOC at depth below the surface sediment of the fiberbank.

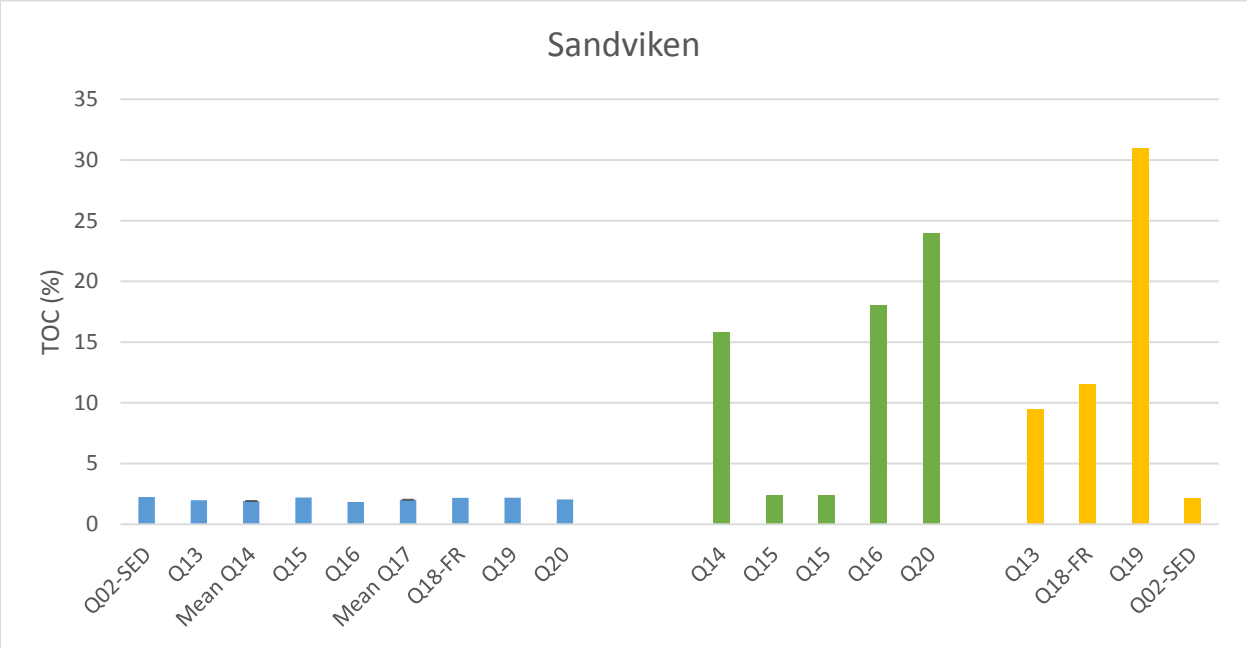


Figure 10 *Total organic carbon (%) found in sediment samples from Sandviken's fiberbanks. Blue samples representing depth of 0 to 4 cm; green samples from 12 to 20 cm and yellow samples from 24 to 32 cm. SED = pure sediment location and FR = fiber-rich sediment location according to the SGU map.*

Väja shows a different TOC profile compared to Sandviken (Figure 11). First off, the surface sediment (0 to 4 cm depth, blue group) displays a TOC ranging from 4.9 to 12 %. In the green group of samples (16 to 20 and 0 to 25 cm depth), the TOC was found to be between 3.7 and 37 %. For the sediment samples from 24 to 32 cm and 0 to 50 cm depth (yellow group) the TOC content ranged between 10 and 39 %. The TOC found in Väja's fiberbank is considerably higher than found in Sandviken. This can be explained by the nature of the material forming the two fiberbanks. For Väja, cellulose fibers are the predominant material found in the fiberbank with some wooden splinters, while in Sandviken, wooden splinters and chips forms the bulk of the fiberbank. Another important observation comes from the layer of deposited clay on Sandviken's fiberbank (~10 cm) (Apler *et al.*, 2014), which has contributed to lowering the TOC content in the surface sediment in Sandviken, to a greater extent than compared to Väja where over sedimentation of clay is less apparent.

Surface samples from the sites within the fiberbank boundary (R13, 14, 15 and 16) held higher TOC than sites from fiber-rich area (R17,19, 20 and 26). Deeper sediment samples considered from the fiber-rich area possessed an TOC ranging from 10 to 22 % (with the exception of R20 at 36 %). Deeper samples from fiberbank area (R 13-16; 18; 21; 23-25) ranged between 3.7 to 39 %, where sites from R13, 14, 15, 16 and 25 contained more than 14 % TOC.

When looking at the yellow group, one can see great variation in TOC. The samples with highest TOC (R18, R20, R22, R23 and R24) are the ones that were sampled at depth 0-50 cm depth and sampled within the fiberbank (R20 situated in fiber-rich), while the samples with lowest TOC (R14, R19 and R26) are sampled at depth of 24-32 cm and sampled within the fiber-rich area

(R14 situated in the fiberbank). The results from both Sandviken and Väja demonstrate that the spatial variation of TOC at a certain depth can be quite heterogeneous and does not necessarily correlate with inventoried type of sediment; fiberbank and fiber-rich sediment.

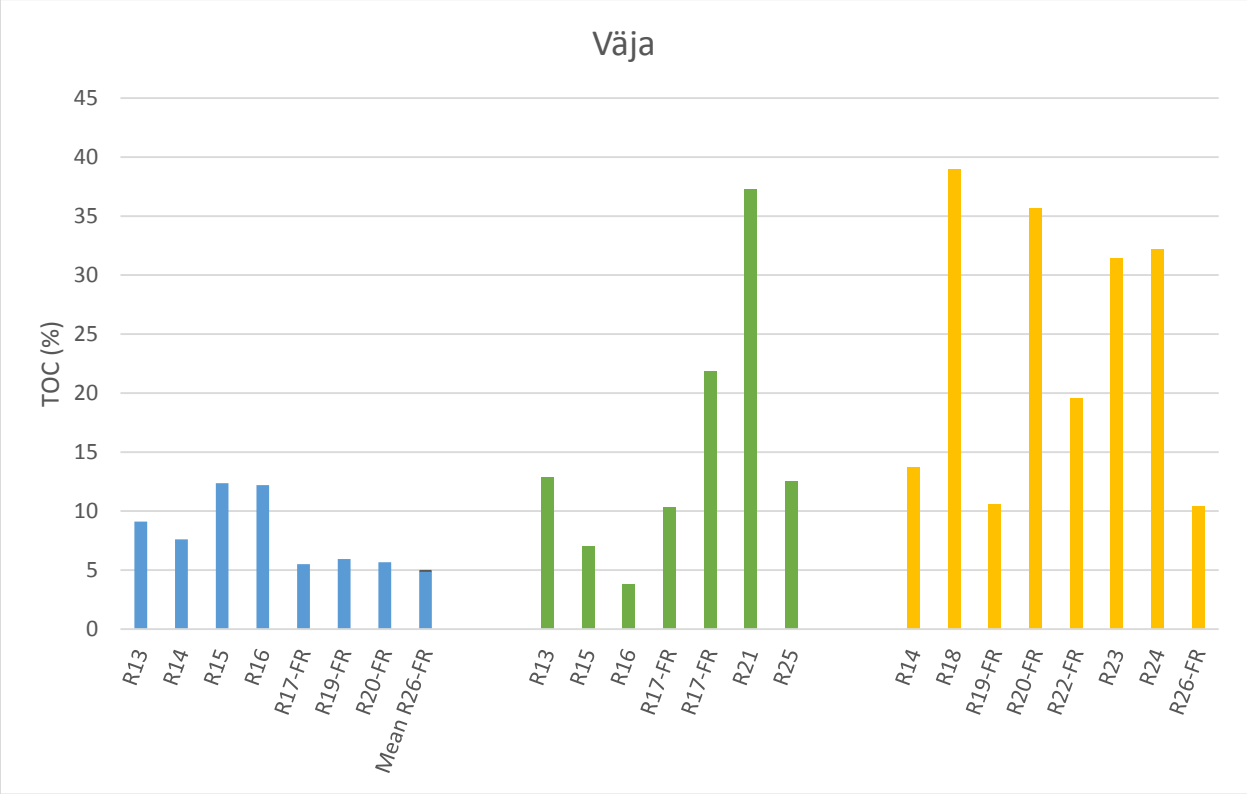


Figure 11 *Total organic carbon (%) found in sediment samples from Väja's fiberbanks. Blue samples representing depth of 0 to 4 cm; green samples from 16 to 20cm and 0 to 25 cm and yellow samples from 24 to 32 cm and 0 to 50 cm. FR = fiber-rich sediment location according to the SGU map.*

Sediment POPs concentration

Sandviken

The concentration of POPs found in each sediment sample are presented on dry weight basis (ng/g DW) in Figure 12 and on TOC basis (ng/g TOC) in Figure 13. In Sandviken, the surface sediment samples exhibit much lower concentrations for all the compounds group, on a dry weight basis, than at greater depth (Figure 12). For all the samples taken in Sandviken, HCB levels ranged between 0.016-1.2 ng/g DW. For the DDX compounds, concentrations ranged between 0.13-72 ng/g DW where the highest concentrations were found in deepest sediment samples from the fiberbank and the fiber-rich area. Concerning Σ_{20}PCBs, the levels ranged between 0.82-200 ng/g DW. Higher levels of PCBs were found with increasing depth of the fiberbank and fiber-rich sediments, with the exception of site Q15 (duplicate sample).

Overall, there isn't much variation from the contamination levels between fiberbank and fiber-rich sediment samples in Sandviken. Despite the resemblance between levels of POPs in the two sediment type, only one site belongs to the fiber-rich sediments type, and thus may not depict what the variance of pollution levels could be in this area. When addressing the pure sediment type (Q02), a rather drastic decrease in concentrations occurs, possibly due to its location far

from the pollution source. Moreover, the duplicate samples from the fiberbank site Q15 (12-20 cm depth) shows some anomalies regarding their levels of pollutants, that it substantially low compared to its peers at a similar depth. These two duplicates depict POPs content and TOC that resembles contents from surface sediment samples. This could potentially be due to a small depression or “pothole” filled by deposited sediment which would extend the surface sediment characteristic of the fiberbank down to 20 cm or more.

When the POPs concentrations were normalized to sediment TOC, the difference in POPs concentrations seem to have become less extreme (Figure 13). First off, the levels in the surface sediment samples are more apparent than on a dry weight basis. Furthermore, site Q17 showed a Σ_{20}PCBs (410 ng/g TOC) equivalent to the levels of PCBs found at moderate to deep depth samples, which was not the case on a dry weight basis. Site Q14 (12-20 cm depth) had the highest amount of PCBs in the sample population with 1300 ng/g TOC, which is nearly 100% more than the levels found in the second highest concentration of Σ_{20}PCBs (680 ng/g TOC) from site Q18-FR.
The HCB content, on a TOC basis, did not differ visually, from the content found on a dry weight basis in figure 12. The levels of DDX are more attenuated in the moderate depth group, compared to the dry weight basis and shifted to higher levels in the deeper depth group, such that site Q02-SED became the third most polluted site.

When assessing the variation of concentration levels by depth, similar behavior is found in figure 12, where deepest sediment samples hold higher content of POPs compared to the surface sediment. Additionally, duplicate samples from site Q15 present the same characteristic as mentioned earlier, which could support the idea of surface sediment extending deeper in the fiberbank at that location. The POPs levels from sites Q19 and Q20 are the only ones that decreased when normalized on TOC. This could be attributed to their high amount of TOC, 31 and 24 % respectively.

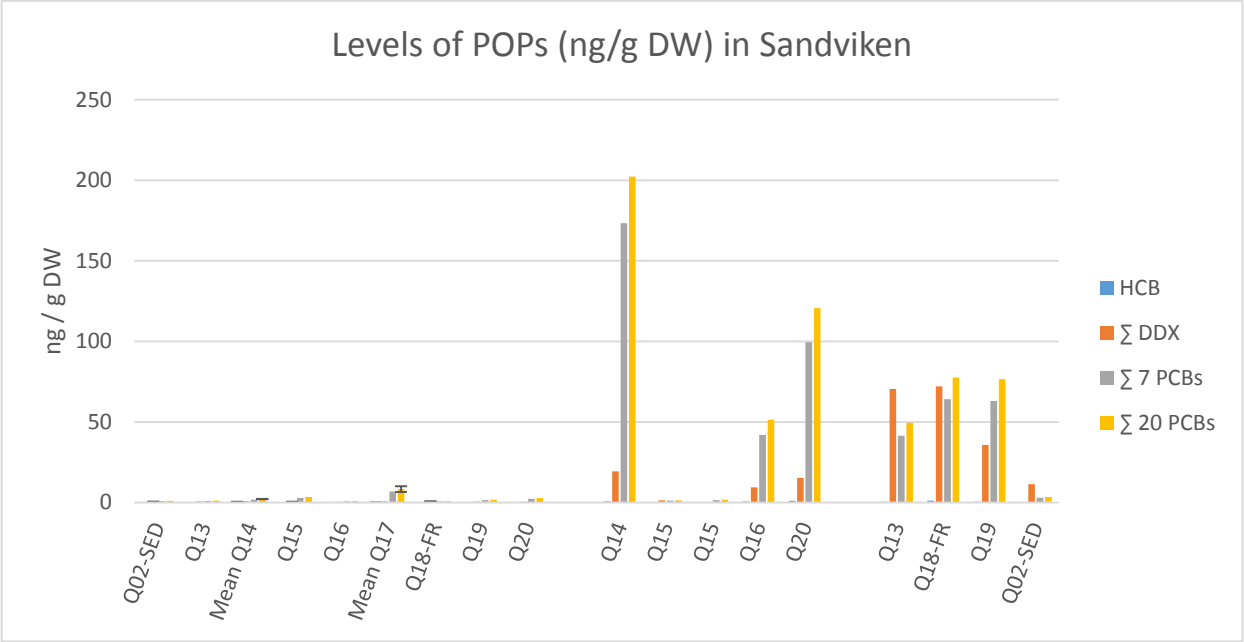


Figure 12 *POP concentrations (ng/g DW), for all sites in Sandviken, grouped by depth of sampling. Left hand side: surface samples (0-4 cm); the middle group: samples of moderate depth (12 to 20 cm) and right hand side: samples taken a greater depth (24 to 32 cm). SED = pure sediment location and FR = fiber-rich sediment location according to the SGU map. Error bars show the standard deviation for triplicate samples.*

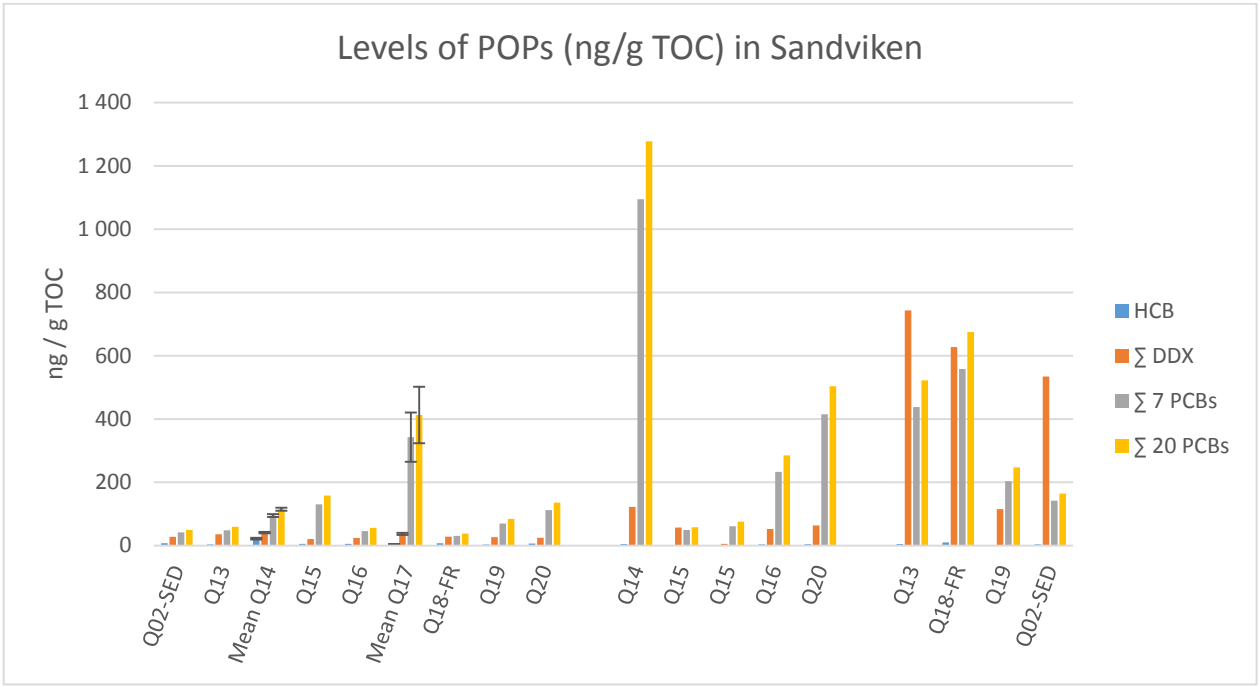


Figure 13 *POP concentrations (ng/g TOC), for all sites in Sandviken, grouped by depth of sampling. Left hand side: surface samples (0-4 cm); the middle group: samples of moderate depth (12 to 20 cm) and right hand side: samples taken a greater depth (24 to 32cm). SED = pure sediment location and FR = fiber-rich sediment location according to the SGU map. Error bars show the standard deviation for triplicate samples.*

Väja

The concentration of POPs found in each sediment sample are presented on dry weight basis (ng/g DW) in Figure 14 and on TOC basis (ng/g TOC) in Figure 15. In Väja more sites with high contamination levels were found (Figure 14). In the surface samples, sites R14, R17-FR and R20-FR contained levels of POPs relatable to contents found at deeper depth in Väja. HCB was found to be present low in concentration (range 0.015-1.5 ng/g DW), in relation to the other compounds (Σ_{20}PCBs 0.35-160 ng/g DW, ΣDDX 0.13-95 ng/g DW). The DDX compounds were found in greater concentration at increasing depth, with highest value found on site R14 and R25 (25 ng/g DW). Regarding the sum of PCBs, many site exhibit levels above 40 ng/g DW, both from moderate to deeper depth samples. A special case arises from duplicate site sample R17-FR, where one of the sample present extremely high values of POPs, while the other sample shows substantially lower POPs content. This case suggests that a great spatial variation can occur even in a very short distance of sampling.

When assessing the very low contaminant levels found at the deepest depth of site R20-FR, R22-FR, R23 and R24, one cannot justify this behavior to the extension of surface sediment in depth, as mentioned for some sites in Sandviken, since all their respective TOC content were considerably higher than all surface sediment samples. Instead, a potential factor for the low concentration may be explained by the sampling method, where sites R22-FR, R23-FR and R24-FR contains sediment samples from 0 to 50 cm depth. Hence, the POPs concentration in these samples show an average value of both surface and deeper sediment. Since surface sediment generally seem to contain lower levels of POPs, the presence of surface sediment could lower the average values in sample R22-FR, R23-FR and R24-FR. Unfortunately, no reference surface samples were taken from those site for comparison to confirm this. Furthermore, the concentrations found at Väja demonstrate a spatial variation that fluctuates greatly regardless of sediment type.

When the POPs concentrations were normalized to sediment TOC (Figure 15), the differences between sites seem to be accentuated. In the surface sediment samples, the most contaminated sites (R14, R17-FR and R20-FR) are more apparent than before. Site R15 and R17-FR, from the moderate sample depth group, showed the highest levels of PCBs (Σ_{20}PCBs >1400 ng/g TOC). Also from that group, site R17-FR and R25 had the highest DDX concentration (>750 ng/g TOC). A major shift in concentration pattern after normalization with TOC was also observed for sites R21 and R18. Previously, on a DW basis, these two sites had moderately high PCBs and DDX values but once based on TOC, their content dropped to a much lower level, presumably explained by their high TOC content (> 35 %). With respect to sediment type, normalization of POPs concentrations to TOC did not affect the spatial variation. The fluctuation in contaminant levels between sites, depth and sediment type is still present.

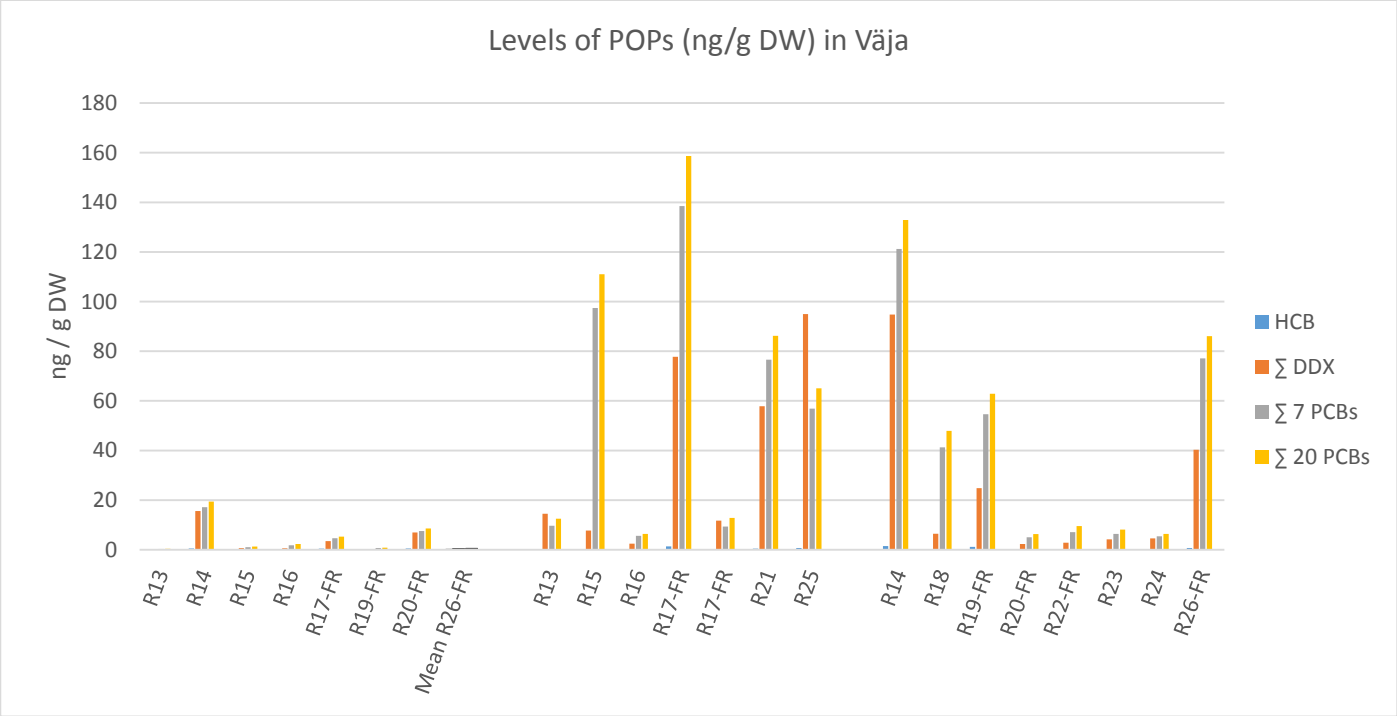


Figure 14 *POP concentrations (ng/g DW), for all sites in Väja, grouped by depth of sampling. Left hand side: surface samples (0-4 cm); the middle group: samples of moderate depth (16 to 20 cm and 0 to 25 cm) and right hand side: samples taken a greater depth (24 to 32 cm and 0 to 50 cm) FR = fiber-rich sediment location according to the SGU map.*

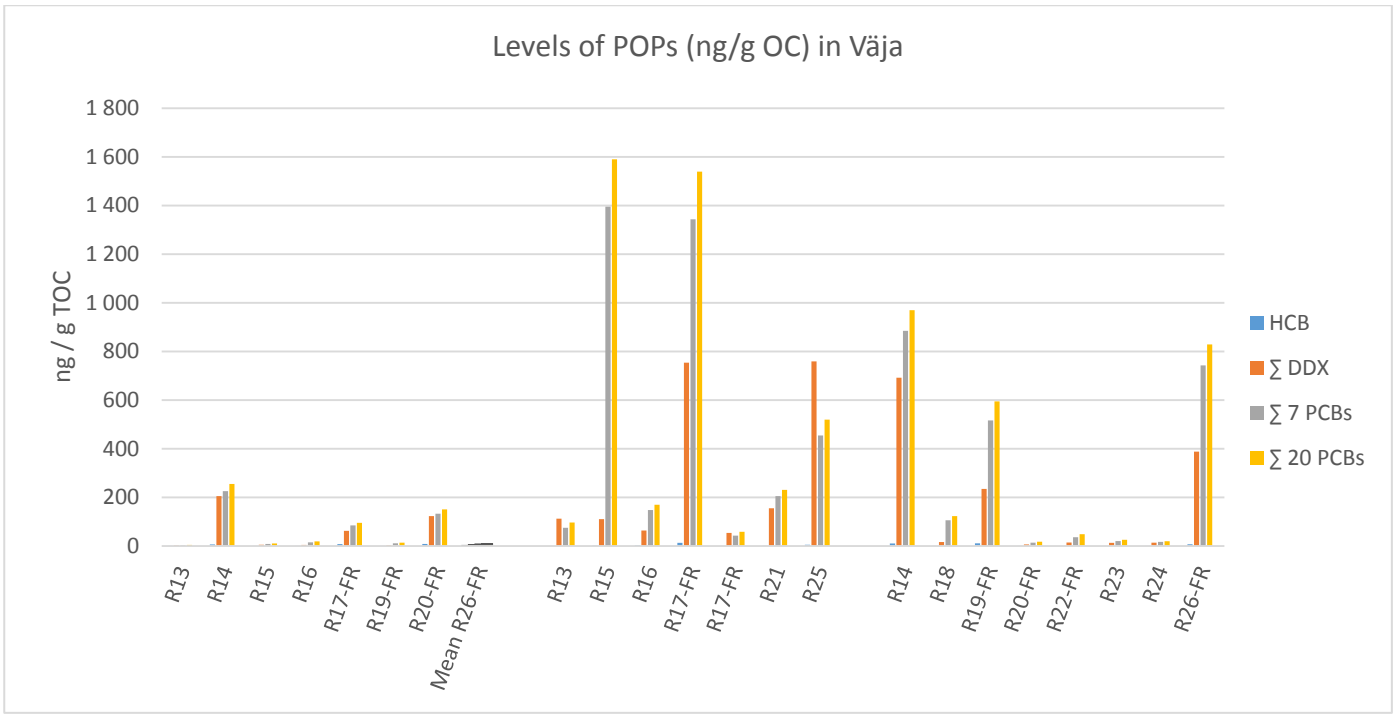


Figure 15 *POP concentrations (ng/g TOC), for all sites in Väja, grouped by depth of sampling. Left hand side: surface samples (0-4 cm); the middle group: samples of moderate depth (16 to 20 cm and 0 to 25 cm) and right hand side: samples taken a greater depth (24 to 32 cm and 0 to 50 cm). FR = fiber-rich sediment location according to the SGU map.*

Classification of sediment

The concentration levels of POPs, on a dry weight basis, was used to classify the contaminants levels according to the Swedish assessment criteria for organic pollutants in sediment along the Swedish coast. The classification is made of five classes that ranges from very low levels to very high levels of contaminants. It is not a classification of toxicity, but rather describes the level of contaminants in sediments according to a population of samples (n = ~500) from different station (n = ~480) in Sweden (*Josefsson*, 2017). Thus, this classification of organic pollutants in sediment is based on statistical distribution of measured concentration in fine-grained surface sediment for Swedish coastal and off-shore areas (*Josefsson*, 2017). The concerned contaminants, covered by the classification, includes HCB, the sum of 7 PCBs (PCB 28; 52; 101;118; 138; 153 and 180) and the sum of *p, p'*-DDX (*p, p'*-DDT; *p, p'*-DDD and *p, p'*-DDE). Table 3 shows the statistical distribution and classification of sediment contaminant levels expressed as ng/g DW.

Table 3 *Swedish assessment criteria for HCB, Σ_7PCB and Σp,p'-DDT; DDD; DDE in sediments along the Swedish coast expressed as ng/g DW(Josefsson, 2017).*

Subject	Class I Very low level	Class II Low level	Class III Moderate level	Class IV High level	Class V Very high level
Percentile rank	5th percentile	25th percentile	25-75 percentile	75th percentile	95th percentile
HCB	<0.020	0.020–0.15	0.15–0.45	0.45–1,6	≥1.6
Σ_7PCB	>0.81	0.81-2.5	2.5-7.6	7.6–34	≥34
Σ*p,p'*-DDX	>0.32	0.32-0.89	0.89–3.5	3.5–10	≥10

In Sandviken (Table 4), the HCB levels in the surface sediment, are mostly classified as low levels (Class II) with site Q02, Q14 and Q18 having moderate levels (Class III). As the depth increase in the fiberbank, the majority of the sites are classified as having high levels (Class IV). For the sum of *p,p'*-DDX, all surface samples are classified as low (Class I) or very low levels (Class II). Whereas, the levels in sediment samples collected at deeper depths are classified as high (Class IV) or very high levels (Class V) except for site Q15. Regarding Σ_7PCB, most surface sediment samples sites are classified as low levels (Class II). However, as the depth increased most sites are categorized as having very high levels (Class V) of PCBs.

Väja (Table 5) display a more heterogeneous pattern of classification among sites, when grouped by depth. To begin with, HCB concentrations from surface samples are mostly classified as having low levels (Class II), whereas site R14 and R20 had high levels (Class IV). When sampling more in depth, nearly half the sites contained low levels (Class II) and the other moderate (Class III) to high levels (Class IV) of HCB. The sum of *p,p'*-DDX for surface samples are categorized as very low levels (Class I), with the exception of R14 which contained high levels (Class IV) of *p,p'*-DDX. At increased depth, half the samples were categorized as having high (Class IV) or very high levels (Class V). For the sum PCB_7, surface sediment samples had very low (Class I) to low levels (Class II), with the exception of site R14 having high levels (Class IV). With increasing depth, the site classification ranges between moderate (Class III) to very high levels (Class V) with the majority of the site categorized as class V.

Table 4 *Classification of sediment samples from Sandviken according to the Swedish assessment criteria for organic pollutants in sediment along the Swedish coast, based on their level of contaminants expressed as ng/g DW. SED = pure sediment location and FR = fiber-rich sediment location according to the SGU map.*

Sample Site	Sample Depth (cm)	HCB	Σ*p,p'*-DDX	Σ_7PCB
Q02-SED	0-4	0.17	0.40	0.94
Q13	0-4	0.077	0.35	0.96
Mean Q14	0-4	0.42 ± 0.052	0.46 ± 0.015	1.8 ± 0.084
Q15	0-4	0.12	0.45	2.9
Q16	0-4	0.10	0.27	0.84
Mean Q17	0-4	0.08 ± 0.0054	0.44 ± 0.031	6.9 ± 1.6
Q18-FR	0-4	0.17	0.50	0.67
Q19	0-4	0.083	0.50	1.5
Q20	0-4	0.14	0.43	2.3
Q14	16-20	0.84	16	173
Q15	17-21	0.047	0.89	1.2
Q15	17-21	0.016	0.12	1.5
Q16	12-16	0.71	4.7	42
Q20	16-20	1.1	13	100
Q13	28-32	0.47	32	42
Q18-FR	24-28	1.2	57	64
Q19	28-32	0.55	35	63
Q02-SED	28-32	0.087	9.0	3.0

Table 5 *Classification of sediment samples from Väja according to the Swedish assessment criteria for organic pollutants in sediment along the Swedish coast, based on their level of contaminants expressed as ng/g DW. FR = fiber-rich sediment location according to the SGU map.*

Sample Site	Sample Depth (cm)	HCB	Σ*p,p'*-DDX	Σ_7PCB
R13	0-4	0.016	0.14	0.33
R14	0-4	0.53	4.3	17
R15	0-4	0.046	0.16	1.1
R16	0-4	0.054	0.18	1.8
R17-FR	0-4	0.42	1.3	4.7
R19-FR	0-4	0.047	0.13	0.68
R20-FR	0-4	0.48	1.8	7.6
Mean R26-FR	0-4	0.023 ± 0.0015	0.066 ± 0.0074	0.27 ± 0.016
R13	16-20	0.090	7.4	9.7
R15	16-20	0.16	3.3	97
R16	15-18	0.12	0.68	5.6

R17-FR	16-20	1.4	31	139
R17-FR	16-20	0.14	5.2	9.4
R21	0-25	0.47	26	77
R25	0-13	0.70	13	57
R14	24-28	1.5	25	121
R18	15-50	0.20	2.7	41
R19-FR	24-28	1.2	11	55
R20-FR	28-32	0.015	0.82	5.0
R22-FR	0-50	0.066	0.86	7.1
R23	0-50	0.040	0.68	6.4
R24	0-50	0.047	1.3	5.4
R26-FR	28-32	0.74	9.4	77

Congeners distribution

PCB

The PCB congeners profile between sites and samples are presented for Sandviken and Väja in Figure 16 and Figure 17, respectively.

In Sandviken, the PCBs show a very similar composition throughout the sites (Figure 16). The PCBs present at highest ratio are PCB-101, PCB-153 and PCB-138. Those three PCBs ratios represents a geometric mean of 22 % (SD = 3 %), 16 % (SD = 2 %) and 25 % (SD = 3 %), respectively, together comprising 6 3% of Σ_{20} PCBs. This finding is in agreement with a previous study which also found these three PCB congeners to be the dominating ones comprising 63 % of Σ_{20}PCBs, in both Sandviken and Väja's fiberbank (Vogel, 2015). Moreover, in this study PCB-28 was found to be present in all surface sediment samples but was detected for only two sites (Q15 and Q02-SED) for the deeper depth sample.

In Väja, the general PCB pattern is also quite similar throughout sites (Fig.17). Similar as in Sandviken, PCB-101, PCB-153 and PCB-138 are present at highest ratios, together comprising 65% of Σ_{20} PCBs. However, the ratio between those three PCBs has changed slightly compared to Sandviken. In Väja, PCB-101, PCB-153 and PCB-138 represents 12 % (SD = 2 %), 24 % (SD = 4 %) and 29 % (SD = 3 %), respectively. Additionally, PCB-180 can be added to the main composition of Väja's PCB with a geometric mean ratio of 9 % (SD = 3 %), whereas in Sandviken PCB-180 represented only 4 % (SD = 1 %). PCB 28 was found in nearly all samples in Väja, not only in the surface samples like in Sandviken.

The results from the distribution ratios of PCBs, for both Sandviken and Väja, suggest that the composition of the technical grade products used by the pulp and paper factories could be different. Moreover, sediment type, fiberbank, fiber-rich and pure sediment, did not influence the distribution ratio of the PCBs in both areas.

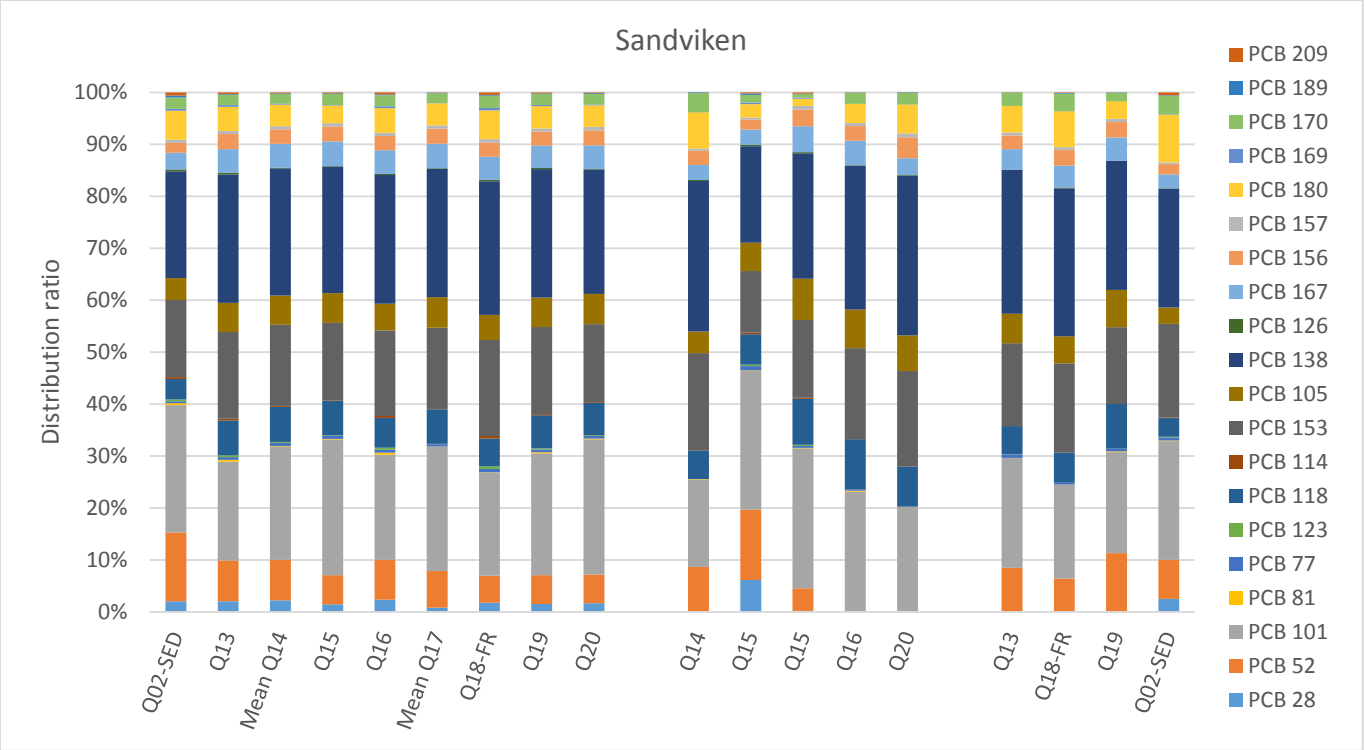


Figure 16 *Distribution ratio of all 20 PCBs for all sites in Sandviken, grouped by depth of sampling. From left to right: 0-4 cm; 12 to 20 cm and 24 to 32 cm. SED = pure sediment location and FR = fiber-rich sediment location according to the SGU map.*

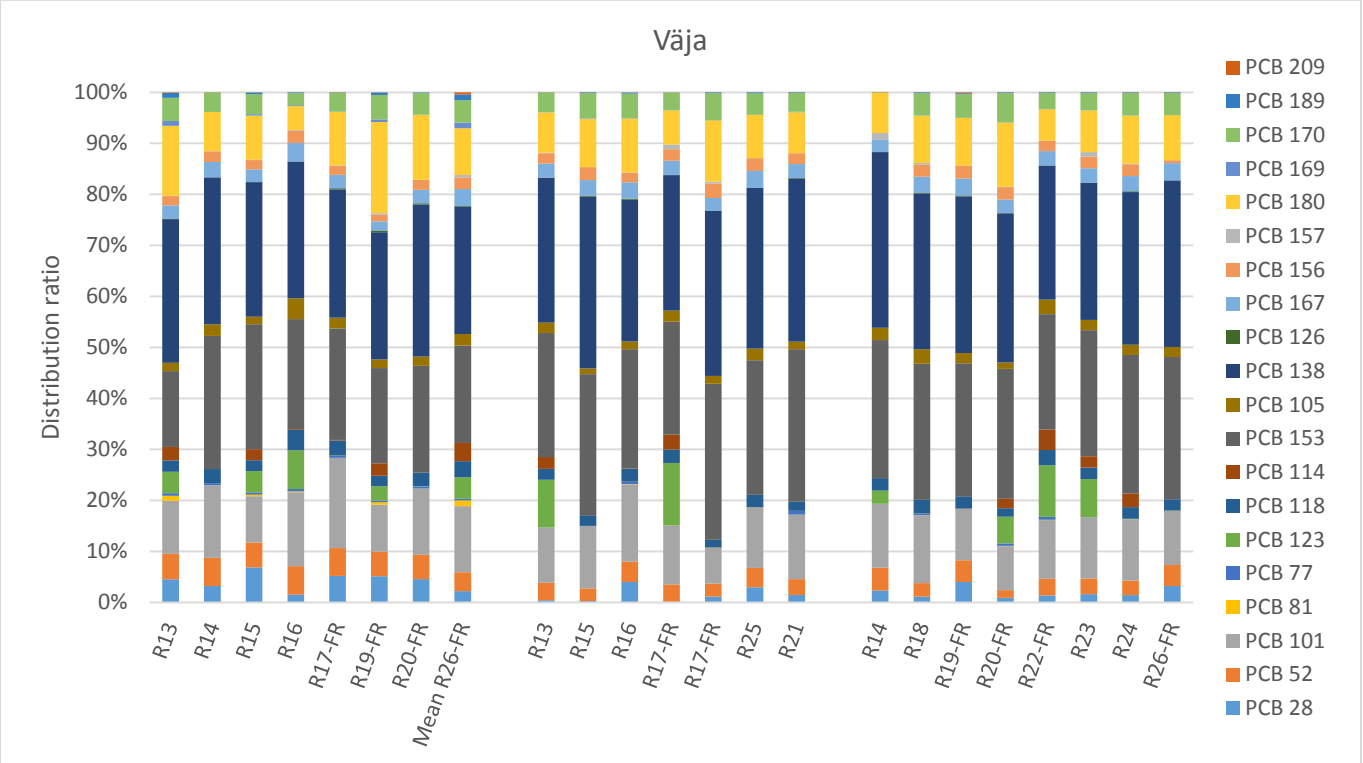


Figure 17 *Distribution ratio of all 20 PCBs for all sites in Väja, grouped by depth of sampling. From left to right: 0-4 cm; 16 to 20 cm & 0 to 25 cm and 24 to 32 cm & 0 to 50 cm. FR = fiber-rich sediment location according to the SGU map.*

DDX

The DDX profile between sites and samples are presented for Sandviken and Väja in Figure 18 and Figure 19, respectively.

In Sandviken, the DDX composition differs between samples (Figure. 18). Whilst the dominant congeners were found to be *p,p'*-DDD and *p,p'*-DDE, with respective geometric mean ratios of 33 % (SD = 21 %) and 19 % (SD = 9%), some samples exhibited large ratios of *o,p'*-DDT, accounting for 18 to 48 % of the total distribution. A previous study also found *p,p'*-DDD and *p,p'*-DDE to be the dominating DDX congeners in Sandviken's fiberbank, together comprising up to 79 % of sum DDX (Vogel, 2015).The surface samples in Sandviken manifest a relatively homogeneous presence of DDE, ranging between 20 and 35 %, when compared to sediment samples taken at deeper depth. Also, the ratio of DDE in samples decreases with depth, being replaced by DDD congeners, indicating lower oxygen content, which favors reductive dechlorination of DDT. However, DDT was also found in deeper sediment as shown in site Q16, where the DDT isomers comprised 80 % of ΣDDX. Since Sandviken's pulp and paper factory has been inactive since 1979, the overall low proportion of DDT isomers reflects historical use of DDT and the age of the fiberbank.

The fiberbank in Väja present a distribution that is more homogeneous throughout sites (Figure 19). In comparison to Sandviken, where *p,p'*-DDD was the predominant isomer, Väja's ratio of *o,p'*-DDD comprised on average 42 % (SD= 18 %) of ΣDDX. This is in agreement with previous findings, where *o,p'*-DDD were found to be the major DDX congener (51 %) in Väja's fiberbank (Vogel, 2015). A plausible reason for that observation may resolve around the use of different DDT-containing products. The concentration of *o,p'*-DDD in Väja could be related to the use of Dicofol, which contained an average of 11 % *o,p'*-DDT and 1.7 % *p,p'*-DDT, when synthesized from technical grade DDT (Qui *et al.*, 2005 & Wong *et al.*, 2009). The high distribution ratio of DDD isomers (mean = 63 %) is expected in a highly anoxic environment. Whereas DDE isomers, produced under aerobic conditions, represents a lower proportion in Väja (geometric mean = 11 %), with higher percentage in surface sediment samples. As for the PCB distribution ratio, the DDX distribution ratio, for both Sandviken and Väja, was not affected by sediment type.

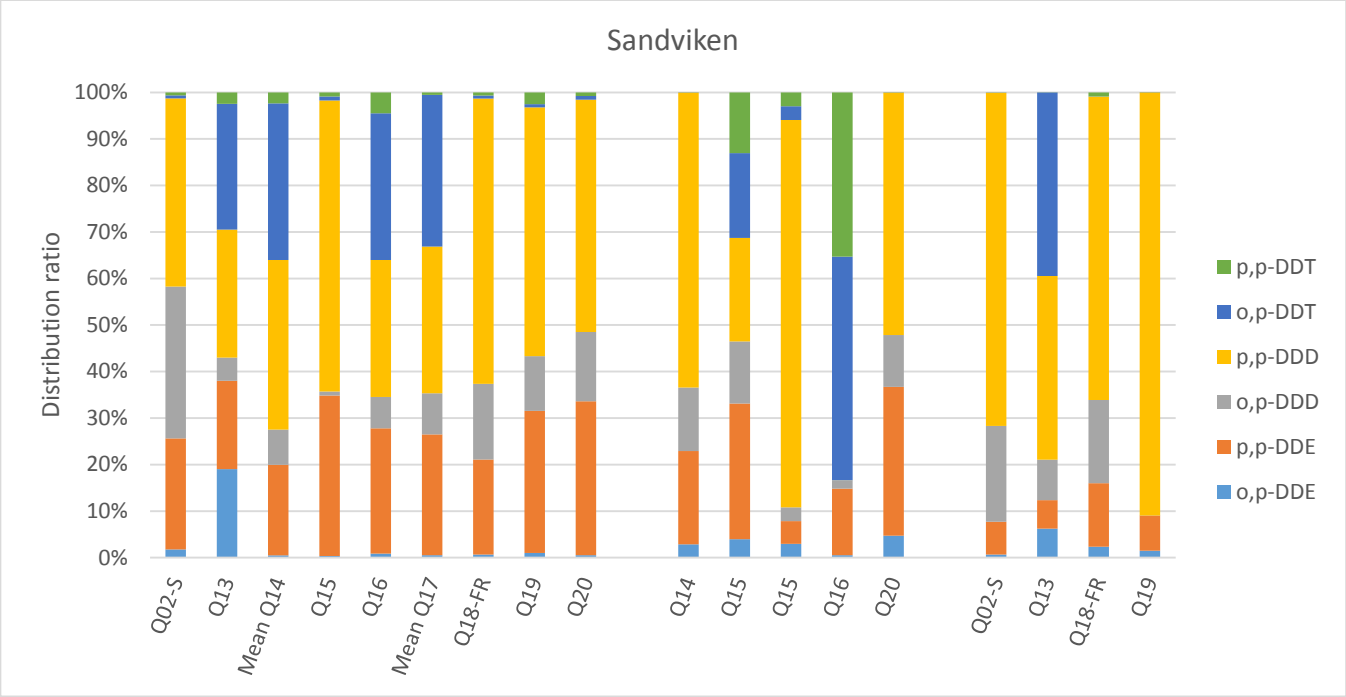


Figure 18 *Distribution ratio of all 6 DDX for all sites in Sandviken, grouped by depth of sampling. From left to right: 0-4 cm; 12 to 20 cm and 24 to 32 cm. SED = pure sediment location and FR = fiber-rich sediment location according to the SGU map.*

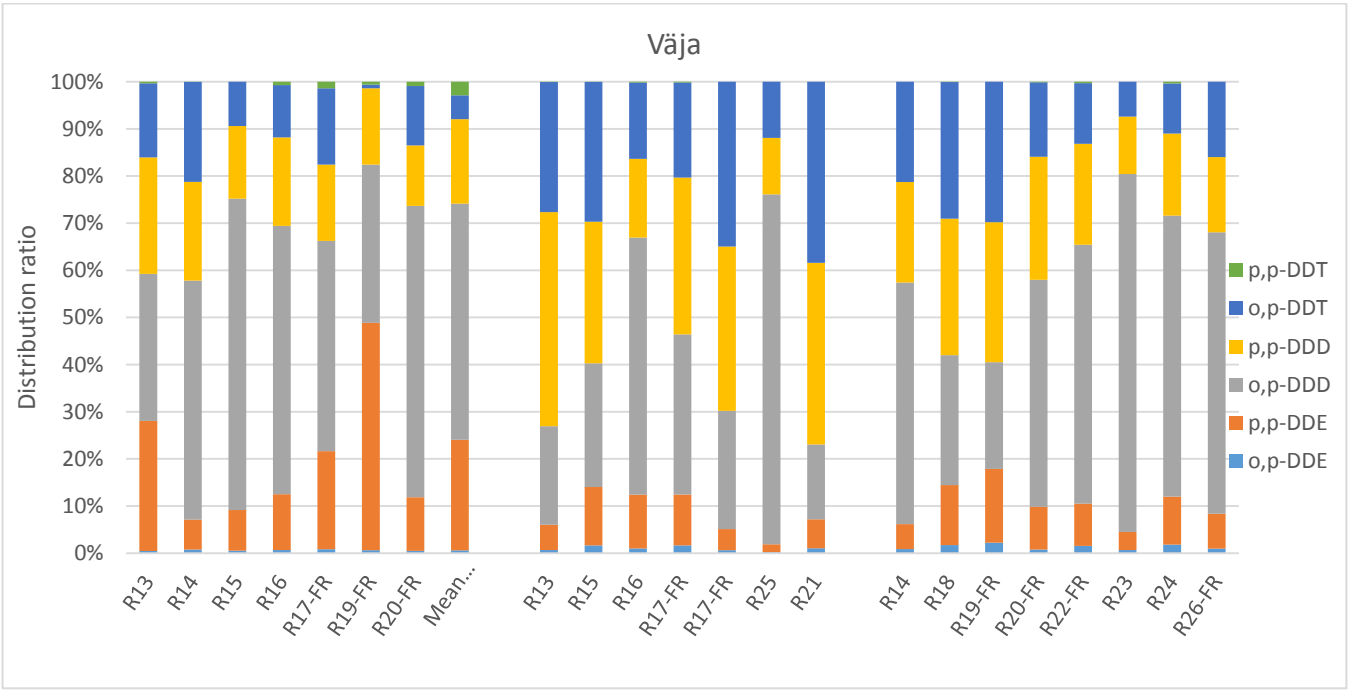


Figure 19 *Distribution ratio of all 6 DDX for all sites in Väja, grouped by depth of sampling. From left to right: 0-4 cm; 16 to 20 cm & 0 to 25 cm and 24 to 32 cm & 0 to 50 cm. FR = fiber-rich sediment location according to the SGU map.*

Technical products / hierarchical clustering analysis

In this section, a correlation analysis between the PCB composition of each sediment sample with 12 known technical PCB products was made, in order to identify the relationship between potential products used and the contamination of the fiberbanks. The idea behind this process is to find out which product could be responsible for the contaminant pattern in the fiberbank sediments. A dendrogram was produced using Simca statistical software to illustrate this by hierarchical clustering. In this way, the samples are clustered together with their closest technical product as can be seen in Figure 20 and Figure 21.

Figure 20 shows the dendrogram made for Sandviken. It is divided in 5 groups, where products and samples of similar properties are clustered. From Sandviken's dendrogram, one can conclude that most samples found in Sandviken are closely related to the product called Kanechlor KC500, represented by group 5. Furthermore, group 5 has two sub-branches, the right-hand side is composed of samples that are more similar in composition to Kanechlor KC500 than the left-hand side. A trend is also found in the sub-branches, where samples from surface depth (S) are mostly grouped on the left branch and samples from a deeper depth (D) grouped on the right side. The sample triplicate Q17-S, duplicate Q15-D and Q02-D are the exception to the trend seen. Additionally, four surface sediment samples from site Q02, Q13, Q16 and Q18 showed a different pattern and are found in group 3. This may suggest that a recent and more local deposition might have occurred and altered the composition of the PCBs, since their respective samples at a deeper depth were found in group 5.

Väja's fiberbanks sediments showed a different composition in PCB's than Sandviken. In Väja's dendrogram (Figure 21), the sediment samples are clustered in three groups, implying different compositions. The largest pool of samples, group 5, demonstrate its resemblance to three technical grade products: Clophen A60, Aroclor 1260 and Kanechlor KC-600. For group 3 and 4, their composition was not match with any products. In group 3, all three sample triplicate from R26-S can be found together with sample R13-S. Nevertheless, their respective depth sample are found in other groups such as, group 4 for R13-S and group 5 for R26-S.

Group 4 presents samples that are from different sites and mostly from deeper depth in the fiberbanks, with the exception of R16-S. Furthermore, their respective surface samples were clustered with group 5 indicating a composition similar to the known PCB products used. This trend is different than the one found in Sandviken, where local and recent deposition may have altered the composition of the surface sediment.

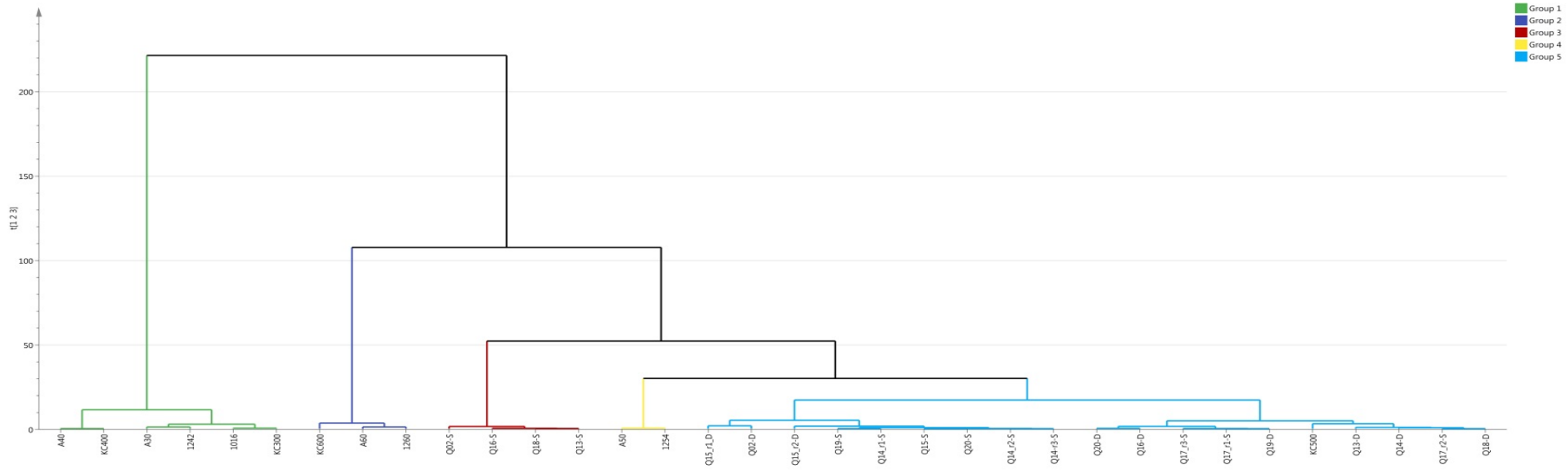


Figure 20 *Dendrogram Sandviken*

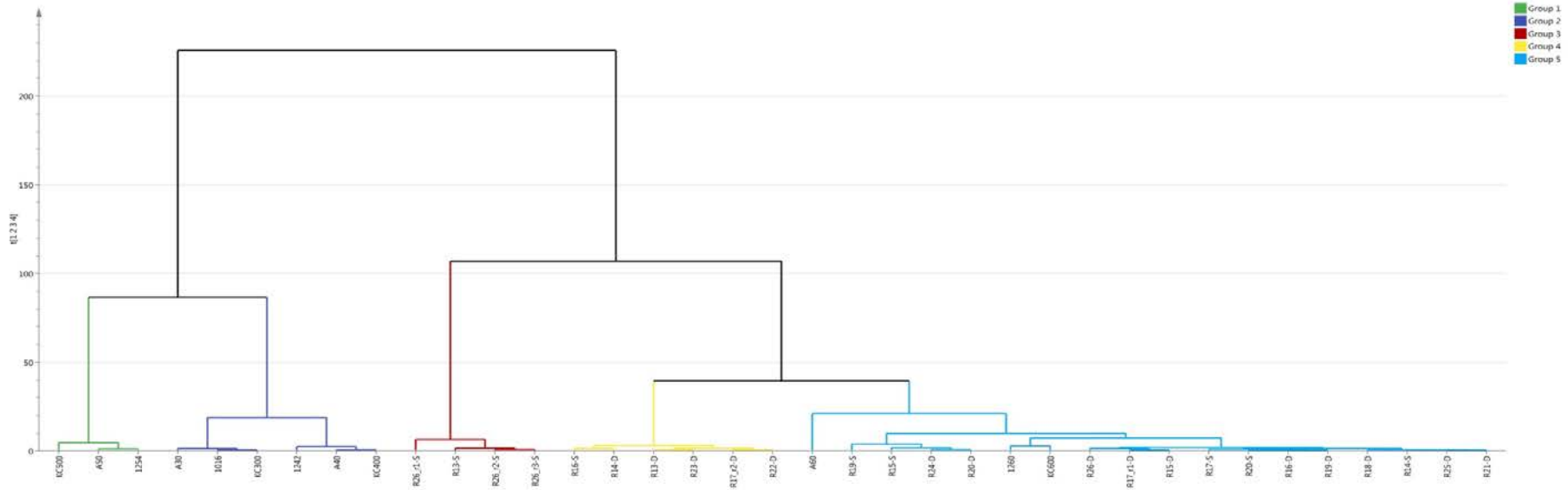


Figure 21 *Dendrogram Väja*

Risk evaluation / Norwegian classification

The Norwegian classification system for sediment, shown in Table 6, can be used to assess the environmental toxicity of the sediment concentration found in the study area. The class boundaries, in this classification system, portrays an expected increasing level of damage to sediment dwelling organisms (Miljødirektoratet, 2016). The upper-limit of Class II and Class III complies with the Water Quality Directive: AA-EQS and MAC-EQS (Miljødirektoratet, 2016). Upper limit for Class II refers to the limit of chronic effects on long-term exposure (AA-EQS) and for Class III, to the limit of acute toxic-effects for short-term exposure (MAC-EQS) (Miljødirektoratet, 2016). The upper-limit of Class I describes the background value and the state of the natural state of the ecosystem. In the case of this study, where man-made contaminants are targeted and do not have a natural source, the upper-limit for Class I is set to zero. Lastly, the upper-limit of Class IV is based on the acute toxicity without safety factors (AF) and defines for more extensive acute toxicity (Miljødirektoratet, 2016).

Table 6 *Classification system for contaminants in sediments based on the Norwegian quality standards for water, sediment and biota, based on their level of contaminants expressed as ng/g DW.*

Classification	Class I Background	Class II Good	Class III Medium	Class IV Bad	Class V Very bad
Toxicity	Background level	No toxic effect	Chronic effects of long term exposure	Acute toxic effects of short-term exposure	Extensive toxic effects
Upper limit	Background level	AA-QS, PNEC	MAC-QS, $PNEC_{acute}$	$PNEC_{acute}$* AF1)	
HCB	0	17	61	610	>610
Σ_7PCB	0	4.1	43	430	>430
Σ*p,p'*-DDX and *o,p'*-DDT	0	15 (p,p'-DDT: 6)	165	1647	>1647

The result of the ecotoxicological assessment for Sandviken are summarized in Table 7. The assessment of the surface sediment samples from Sandviken depicts a general good state (Class II) for all POPs, except for site Q17, where the levels of Σ_7PCB are classified as having chronic effects at long term exposure (Class III). At moderate depth, we see that all site reflects a Class II status for HCB concentrations. Only one site (Q14), at moderate depth, was found to be in Class III, regarding its DDX content, while the remaining sites being categorized as Class II. For the Σ_7PCB, two sites, Q14 and Q20, were found to have bad status with acute toxic effects of short-term exposure and one site, Q16, with medium status. For the deep sediment samples, all sites lie within Class II for HCB levels. For ΣDDX, three sites show concentrations reaching chronic effects of long-term exposure (Class III) and only one site with no toxic effect (Class II); belonging to the pure sediment sample site (Q02-SED). The Σ_7PCB in deep sediment samples, showed a medium and bad status for the fiberbank, a bad status for the fiber-rich sample and a good status for the pure sediment sample (Q02-SED).

The general status for the HCB concentration in Sandviken, regarding depth and sediment type seems to fall under the classification of good status or no toxic effect to aquatic organisms. As for the Σ *p,p'*-DDX and *o,p*'-DDT, their concentration seems to increase with depth. Concentrations that can lead to chronic effects of long term exposure are found where the Σ *p,p'*-DDX and *o,p*'-DDT exceeds 24 cm depth (exception for the pure sediment sample). The Σ_7PCB concentrations also seem to increase with depth, where chronic and acute toxic effects of exposure start to occur at depth of over 12 cm.

Table 7 *Classification of sediment samples from Sandviken according to the Norwegian quality standards for water, sediment and biota, based on their level of contaminants expressed as ng/g DW. SED = pure sediment location and FR = fiber-rich sediment location according to the SGU map.*

Sample Site	Sample Depth (cm)	HCB	Σ*p,p'*-DDX and *o,p'*-DDT	Σ_7PCB
Q02-SED	0-4	0.17	0.41	0.94
Q13	0-4	0.077	0.54	0.96
Mean Q14	0-4	0.42 ± 0.052	0.72 ± 0.040	1.8 ± 0.084
Q15	0-4	0.12	0.45	2.9
Q16	0-4	0.10	0.42	0.84
Mean Q17	0-4	0.081 ± 0.0054	0.68 ± 0.048	6.9 ± 1.6
Q18-FR	0-4	0.17	0.51	0.67
Q19	0-4	0.083	0.51	1.5
Q20	0-4	0.14	0.43	2.3
Q14	16-20	0.84	16	173
Q15	17-21	0.047	1.2	1.2
Q15	17-21	0.016	0.13	1.5
Q16	12-16	0.71	9.3	42
Q20	16-20	1.1	13	100
Q13	28-32	0.47	60	42
Q18-FR	24-28	1.2	58	64
Q19	28-32	0.55	35	63
Q02-SED	28-32	0.087	9.0	3.0

The result of the ecotoxicological assessment for Väja are summarized in Table 8. The HCB levels for all sites and sample depth, are classified as having no toxic effects on aquatic and sediment dwelling organisms (Class II). Also the levels of Σ *p,p'*-DDX and *o,p*'-DDT in all surface sediment samples corresponded to a good status and including more than half of the samples (9 out of 15) taken from moderate to deep depth. The remaining six samples, belonging to fiberbank and fiber-rich sites, held contents that could cause chronic effects of long-term exposure (Class III). As for the Σ_7PCB, levels varied between no toxic effects (Class II) and chronic effects of long term exposure (Class III) in surface sediment. From moderate to deeper depth samples, 8 sites were found to be classified as Class III for Σ_7PCB, while 7 sites showed levels inducing acute effects of short-term exposure (Class IV).

Overall, the levels of pollutants in Väja, concerning mostly ∑ *p,p'*-DDX and *o,p'*-DDT and the Σ_7PCB , were found to differ greatly, from site to site, sometimes as much as one order of magnitude within moderate and deeper depth groups. Here again, the POPs contents found in Väja are ambiguous, with respect to their sediment type. Additionally, the spatial variation in this area could be seen as more erratic than in Sandviken, where POPs content were more likely to increase with depth.

In spite of the results given by the Norwegian classification system for sediment, the ecotoxicological limit values employed are adapted to the Norwegian conditions. Those conditions refer to organic carbon content estimated at 1% in the sediments (Miljødirektoratet, 2016), which is lower than what is found in the studied area. Because of the higher TOC nature of the fiberbank and fiber-rich sediment, the contaminants are more sorbed to fiber sediments making them less bioavailable for organism. Consequently, by using the Norwegian classification system, there is a risk of overestimating the ecotoxicological effects of the target contaminants on biota.

Table 8 *Classification of sediment samples from Väja according to the Norwegian quality standards for water, sediment and biota, based on their level of contaminants expressed as ng/g DW. FR = fiber-rich sediment location according to the SGU map.*

Sample Site	Sample Depth (cm)	HCB	Σ*p,p'*-DDX and *o,p'*- DDT	Σ_7PCB
R13	0-4	0.016	0.18	0.33
R14	0-4	0.53	7.6	17
R15	0-4	0.046	0.22	1.1
R16	0-4	0.054	0.24	1.8
R17-FR	0-4	0.42	1.9	4.7
R19-FR	0-4	0.047	0.13	0.68
R20-FR	0-4	0.48	2.6	7.6
Mean R26-FR	0-4	0.023 ± 0.0015	0.073 ± 0.011	0.27 ± 0.016
R13	16-20	0.090	11	9.7
R15	16-20	0.16	5.6	97
R16	15-18	0.12	1.1	5.6
R17-FR	16-20	1.4	58	139
R17-FR	16-20	0.14	7.6	9.4
R21	0-25	0.47	48	77
R25	0-13	0.70	24	57
R14	24-28	1.5	45	121
R18	15-50	0.20	4.6	41
R19-FR	24-28	1.2	19	55
R20-FR	28-32	0.15	1.2	5.0
R22-FR	0-50	0.066	1.2	7.1
R23	0-50	0.040	0.99	6.4
R24	0-50	0.047	1.8	5.4
R26-FR	28-32	0.74	16	77

Conclusion

The results from this study have given valuable information about the characteristics of the contaminated sediments by fiber material from pulp and paper industries in the Ångermanälven estuary. From the data collected in both Sandviken and Väja, the differences between fiberbank and fiber-rich sediments, regarding POPs concentrations and TOC, was not conclusive enough to advocate for a distinction between the two contaminated fibrous sediments. Additionally, the pollution content, from both areas studied, showed that data can be irregular within each fiber-impacted sediment type. Henceforth, the spatial distribution of POPs, on a horizontal plane, can be quite heterogeneous, thus increasing the sample size needed to study them. Total organic carbon content was generally lower in surface sediment due to newly deposited fine material. Furthermore, the quantification of POPs, when analyzed by depth of sampling, revealed that in Sandviken, levels of DDX and PCBs tended to increase with depth, as opposed to Väja, where some discrepancies appeared.

The distribution ratio for PCBs, in both areas, exposed the composition of the pollutants and together with the SIMCA statistical analysis tool, validate their plausible source. Technical grade product Kanechlor KC-500 was similar to the PCB composition of most samples in Sandviken, while Väja's PCB composition were closely related to technical grade product Aroclor 1260, Clophen A60 and Kanechlor KC-600. The composition of DDX, between the two areas, was dominated by DDD isomers, as expected in anoxic environments. The proportion of DDE isomers was found to be greater in surface sediment samples than at deeper depths, manifesting a higher prevalence of aerobic degradation of DDT in this strata. Two contrasting results emerged when comparing both areas. First, the presence of *p,p'*-DDT found to be more persistent in the samples of Väja, all depths included. Second, the predominance of the product *o,p'*-DDD in Väja, as opposed to *p,p'*-DDD in Sandviken, may suggest different sources for the DDX contamination.

The classification of the sediment samples according to the Swedish assessment criteria for organic pollutants in sediment along the Swedish coast, depicted a spectrum of contamination levels ranging from very low to very high contents of POPs, for both areas investigated. Most of the sample were categorized as having high (75^{th} percentile) and very high levels (95^{th} percentile) of POPs, with highest levels found in deeper sediments within the fiberbanks.

On a risk assessment point of view, the classification system from the Norwegian quality standards for sediment revealed the toxicity of the target pollutants found in the studied areas. The levels of HCB were classified as having no effects on biota, for all the samples analyzed. The state for the surface sediment, regarding the Σ *p,p'*-DDX and *o,p'*-DDT, in both areas, was classified as good, with no effects on biota (Class II). At increased depth, many sites contained levels inducing chronic effects of long-term exposure. In Sandviken, the levels of Σ_7PCB in surface sediment samples were measured to have no toxic effects (n = 8), with one site classified as causing chronic effects of long-term exposure. For Väja, 3 out of 9 surface sediment samples were classified as causing chronic effects of long-term exposure. For both Sandviken and Väja, the levels of Σ_7PCB increased with sampling depth, and some sites contained levels which are classified as having acute toxic effects of short-term exposure. Although the likelihood of overestimating the ecotoxicological risk of the Swedish sediments by applying the Norwegian classification is probable, it is still the best classification system for contaminated sediments

available. However, there is still a need for Swedish authorities to develop a risk classification system, for organic rich sediments, to better assess the ecotoxicological risk of fiberbanks.

This study, performed under the research project TREASURE, has contributed in generating important information distribution of hazardous contaminants in fiberbanks, and the risk on immediate environments. The outcome from this study demonstrated how heterogeneous the contaminant levels can be in the vicinity of a pulp and paper factory. This should be taken into consideration when defining remediation strategies for fiber-impacted areas, like delimiting the site of a remediation project.

Acknowledgment

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Appendix

Table 9 *Native compounds used as authentic reference standards. Origin abbreviation: WL=Wellington Laboratories Inc. (Guelph, Not, CAN); CI= Cambridge Isotopes Laboratories Inc. (Andover, MA, USA); SA= Sigma-Aldrich (Steinheim, Germany).*

Acronym	Compound	Origin	Purity	log K_{OW} [a,b]
HCB	Hexachlorobenzene	SA	99%	5.50
o,p'-DDT	2-(2-chlorophenyl)-2-(4-chlorophenyl)-1,1,1-trichloroethane	CI	97%	6.98
p,p'-DDT	2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane	CI	98%	6.19
o,p'-DDE	2-(2-chlorophenyl)-2-(4-chlorophenyl)-1,1-dichloroethene	CI	98%	5.80
p,p'-DDE	2,2-bis(4-chlorophenyl)-1,1-dichloroethene	CI	98%	5.70
o,p'-DDD	2-(2-chlorophenyl)-2-(4-chlorophenyl)-1,1-dichloroethane	CI	98%	6.00
p,p'-DDD	2,2-bis(4-chlorophenyl)-1,1-dichloroethane	CI	98%	5.50
CB-28	2,4,4'-trichlorobiphenyl	WL	≥ 99%	5.67
CB-52	2,2',5,5'-tetrachlorobiphenyl	WL	≥ 99%	5.84
CB-77	3,3',4,4'-tetrachlorobiphenyl	WL	≥ 99%	6.36
CB-81	3,4,4',5-tetrachlorobiphenyl	WL	≥ 99%	6.36
CB-101	2,2'4,5,5'-pentachlorobiphenyl	WL	≥ 99%	6.38
CB-105	2,3,3',4,4'-pentachlorobiphenyl	WL	≥ 99%	6.65
CB-114	2,3,4,4'5-pentachlorobiphenyl	WL	≥ 99%	6.65
CB-118	2,3',4,4'5-pentachlorobiphenyl	WL	≥ 99%	6.74
CB-123	2',3,4,4',5-pentachlorobiphenyl	WL	≥ 99%	6.74
CB-126	3,3',4,4', 5-pentachlorobiphenyl	WL	≥ 99%	6.89
CB-138	2,2',3,4,4',5'-hexachlorobiphenyl	WL	≥ 99%	6.83
CB-153	2,2'4,4'5,5'-hexachlorobiphenyl	WL	≥ 99%	6.92
CB-156	2,3,3',4,4',5-hexachlorobiphenyl	WL	≥ 99%	7.18
CB-157	2,3,3',4,4',5-hexachlorobiphenyl	WL	≥ 99%	7.18
CB-167	2,3',4,4',5,5'-hexachlorobiphenyl	WL	≥ 99%	6.74
CB-169	3,3',4,4',5,5'-hexachlorobiphenyl	WL	≥ 99%	7.42
CB-170	2,2',3,3',4,4',5-hexachlorobiphenyl	WL	≥ 99%	7.27
CB-180	2,2',3,4,4',5,5'-heptachlorobiphenyl	WL	≥ 99%	7.36
CB-189	2,3,3',4,4',5,5'-heptachloro biphenyl	WL	≥ 99%	7.71
CB-209	2,2',3,3',4,4',5,5',6,6'-decachloro biphenyl	CI	98%	8.18

a) Log K_{OW} values for PCBs from Hawker and Connell (1988).
b) Log K_{OW} values for DDX and HCB from Mackay *et al*. (2006).

Table 10 Isotope-(^{13}C)-labelled compounds used as internal standards (IS) or recovery standards (RS). *Origin abbreviation WL=Wellington Laboratories Inc., Guelph, Ont, CAN; CI= Cambridge Isotopes Laboratories Inc., Andover, MA, USA; SA= Sigma-Aldrich (Steinheim, Germany).*

Acronym	Compound	Comment	Origin	Purity
HCB ($^{13}C_6$)	Hexachloro-($^{13}C_6$)-benzene	IS	CI	99%
p,p'-DDT ($^{13}C_{12}$)	2,2-bis(4-chloro-($^{13}C_{12}$)-phenyl)-1,1,1-trichloroethane	IS	CI	99%
p,p'-DDE ($^{13}C_{12}$)	2,2-bis(4-chloro-($^{13}C_{12}$)-phenyl)-1,1-dichloroethene	IS	CI	99%
CB-28 ($^{13}C_{12}$)	2,4,4'-trichloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-52 ($^{13}C_{12}$)	2,2',5,5'-tetrachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-77 ($^{13}C_{12}$)	3,3',4,4'-tetrachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-81 ($^{13}C_{12}$)	3,4,4',5-tetrachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-97 ($^{13}C_{12}$)	2,2',3',4,5-pentachloro-($^{13}C_{12}$)-biphenyl	RS	WL	99%
CB-101 ($^{13}C_{12}$)	2,2'4,5,5'-pentachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-105 ($^{13}C_{12}$)	2,3,3',4,4'-pentachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-114 ($^{13}C_{12}$)	2,3,4,4'5-pentachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-118 ($^{13}C_{12}$)	2,3',4,4'5-pentachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-123 ($^{13}C_{12}$)	2',3,4,4',5-pentachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-126 ($^{13}C_{12}$)	3,3',4,4', 5-pentachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-138 ($^{13}C_{12}$)	2,2',3,4,4',5'-hexachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-153 ($^{13}C_{12}$)	2,2'4,4'5,5'-hexachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-156 ($^{13}C_{12}$)	2,3,3',4,4',5-hexachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-157 ($^{13}C_{12}$)	2,3,3',4,4',5-hexachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-167 ($^{13}C_{12}$)	2,3',4,4',5,5'-hexachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-169 ($^{13}C_{12}$)	3,3',4,4',5,5'-hexachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-170 ($^{13}C_{12}$)	2,2',3,3',4,4',5-hexachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-180 ($^{13}C_{12}$)	2,2',3,4,4',5,5'-heptachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-188 ($^{13}C_{12}$)	2,2',3,4',5,6,6'-heptachloro-($^{13}C_{12}$)-biphenyl	RS	CI	99%
CB-189 ($^{13}C_{12}$)	2,3,3',4,4',5,5'-heptachloro-($^{13}C_{12}$)-biphenyl	IS	WL	≥99%
CB-209 ($^{13}C_{12}$)	2,2',3,3',4,4',5,5',6,6'-decachloro-($^{13}C_{12}$)-biphenyl	IS	CI	99%